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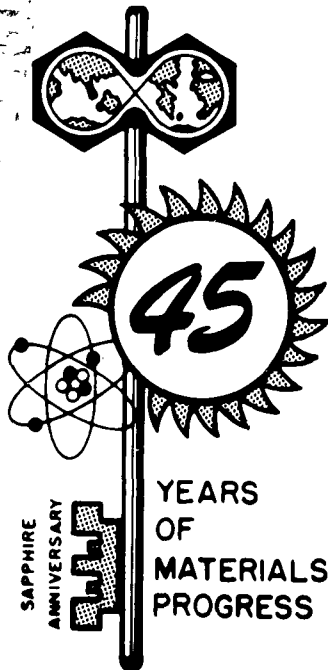
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DIFFUSION IN TITANIUM AND TITANIUM ALLOYS

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by the Armour Research Foundation, Chicago, Illinois;
Rodney P. Elliott, author.)

FOREWORD

This report was prepared by Armour Research Foundation of Illinois Institute of Technology under USAF Contract No. AF 33(616)-7656. This contract was initiated under Project No. 7351, "Metallic Materials," Task No. 735105, "High Strength Metallic Materials." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Mr. Paul L. Hendricks acting as project engineer.

This report covers work conducted during the period 1 November 1960 to 28 February 1962.

The experimental work was carried out under the direction of Rodney P. Elliott, project engineer. Edward A. Howe was project experimentalist. Pertinent data are recorded in ARF Logbooks C 10731, C 11174, and C 11910. The research is identified at Armour Research Foundation as Project No. B 208, with this final technical report designated ARF 2208-16.

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ABSTRACT

The self-diffusion of titanium and the interdiffusion of aluminum, zirconium, molybdenum, vanadium, and oxygen in titanium have been investigated in the temperature range 600°-1300°C. Diffusion couples were prepared by roll-bonding or press-bonding techniques. Electron microprobe methods were used to determine the penetration of the substitutionally dissolved solutes; vacuum fusion analysis was used to determine the penetration of interstitially dissolved oxygen.

The determined diffusion may be summarized:

$$\ln D_T = (-27.14 \pm 1.56) - (11,800 \pm 3,000)/RT \text{ for Zr in } \alpha\text{-Ti}$$

$$\ln D_T = (-4.01 \pm 1.22) - (40,100 \pm 3,300)/RT \text{ for Zr in } \beta\text{-Ti}$$

$$\ln D_T = (-17.19) - (28,400)/RT \text{ for Mo in } \alpha\text{-Ti}$$

$$\ln D_T = (-9.00 \pm 0.92) - (33,100 \pm 2,400)/RT \text{ for Mo in } \beta\text{-Ti}$$

$$\ln D_T = (-31.39) - (3,100)/RT \text{ for V in } \alpha\text{-Ti}$$

$$\ln D_T = (-4.38 \pm 1.04) - (41,400 \pm 2,800)/RT \text{ for V in } \beta\text{-Ti}$$

$$\ln D_T = (-14.94 \pm 1.15) - (16,200 \pm 2,200)/RT \text{ for O in } \alpha\text{-Ti}$$

$$\ln D_T = (+8.37 \pm 2.21) - (66,800 \pm 7,000)/RT \text{ for O in } \beta\text{-Ti}$$

The electron microprobe analysis could not be used to determine the penetration curves of aluminum in titanium because of the very high absorption of characteristic aluminum X-radiation by titanium.

The self-diffusion of titanium was investigated by studying penetration of Ti^{44} , formed by bombarding scandium with protons. Diffusion couples were formed by dissolving Ti^{44} -enriched TiO_2 into the titanium. Self-diffusion of titanium may be summarized:

$$\ln D_T = (-21.08) - (5,700)/RT \text{ for } \alpha\text{-Ti}$$

$$\ln D_T = (-8.40) - (28,600)/RT \text{ for } \beta\text{-Ti}$$

The diffusion equations for molybdenum and vanadium in α -titanium, and for the self-diffusion of titanium must be considered preliminary.

This report has been reviewed and is approved.



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DIFFUSION IN TITANIUM AND TITANIUM ALLOYS

I INTRODUCTION

Diffusion characteristics, atom mobility, and activation energy are basic to all metal processes which involve: (a) the movement of crystal faults; (b) the kinetics of alloy transformation; or (c) the development of composite structures such as clads and laminates. The lack of adequate diffusion data for titanium-based alloys has hampered correlation of known physical phenomena such as nucleation, growth, age hardening, and the martensitic transformations of these alloys with what is probably the controlling factor. It is therefore both scientific and practical to analyze the diffusion characteristics of titanium and titanium alloys.

II LITERATURE SURVEY

To date, little information is available on the diffusion of second metals in titanium, although a fair amount of data is available on interstitial diffusion in titanium. The Titanium Metallurgical Laboratory, in Report No. 21 and a subsequent Memorandum (1, 2), has reviewed both the open literature and Government publications. More recently Peterson (3) has published a critical review of diffusion data for refractory alloys.

Due to the general belief that there is no suitable radioactive isotope, no self-diffusion data for titanium are available in the literature. The activation energy for self-diffusion has been estimated.

- a. An activation energy of 73,600 cal/mol is calculated from the equation of LeClair (4).
- b. Peterson (3) has plotted the activation energy for self-diffusion vs melting temperature from which a value of 72,200 cal/mol is estimated.
- c. Nachtrieb and Handler (5) show the relationship between latent heat of fusion, melting temperature, and activation energy of self-diffusion. From this formula, a value of 73,600 cal/mol is calculated by Peterson (3) for β -Ti. Peterson (3) quotes Kaufman, who has calculated a melting temperature of α -Ti to be approximately the same as β -Ti. From this it is concluded that the activation energy of self-diffusion of α - and β -Ti would be approximately the same.

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- d. Reynolds, Ogden, and Jaffe (6) have inferred the activation energy for self-diffusion of titanium to be approximately 75,300 cal/mol, based on an hypothesis formed for the air contamination of commercial titanium sheet.
- e. Orr, Sherby, and Dorn (7) have calculated the activation energy of self-diffusion to be 60,000 cal/mol from creep studies. Dorn (8) has shown that activation energy for creep is identical with the activation energy for self-diffusion.
- f. Polonis and Parr (9) have estimated an activation energy of self-diffusion of titanium to be 77,000 cal/mol based on a study of decomposition kinetics of titanium-nickel alloys.

Kidson and McGurn (10) have recently determined the self-diffusion coefficient of β -zirconium and show that the observed activation energy is about one half that calculated by such indirect methods as those obtained by the above-listed investigators. Kidson and McGurn cite similar evidence that the activation energy for self-diffusion of γ -uranium, β -titanium, and chromium is about half that calculated by indirect methods. Pound, Bitler, and Paxton (11) have suggested an explanation of such a phenomenon.

Goold (12) has determined diffusion characteristics of aluminum in both α - and β -titanium as a function of temperature, and for molybdenum and vanadium in β -titanium as a function of temperature:

$$\ln D_T = (-11.04) - (23,700)/RT \text{ for Al in } \alpha\text{-Ti}$$

$$\ln D_T = (-11.11) - (21,900)/RT \text{ for Al in } \beta\text{-Ti}$$

$$\ln D_T = (-11.51) - (24,000)/RT \text{ for Mo in } \beta\text{-Ti}$$

$$\ln D_T = (-5.12) - (39,600)/RT \text{ for V in } \beta\text{-Ti}$$

Martens (13) has calculated the activation energy for zirconium in titanium to be 23,000 cal/mol.

Conflicting experimental data are reported for the diffusion coefficients of oxygen in titanium. Wasilewski and Kehl (14) determined the diffusion coefficient of oxygen in β -titanium from measurements of oxygen penetration in a Sieverts apparatus. Large external scale in similar studies for α -titanium precluded calculations of diffusion coefficients by these experimenters since the boundary conditions of the applicable solution to Fick's equation no longer held. Claisse and Koenig (15) have studied the effect of oxygen diffusion in β -titanium under the influence of an electric field. Their data are significantly different from those of Wasilewski and Kehl. Pratt, Bratina, and Chalmers (16), in addition to Wasilewski and Kehl, have estimated that the diffusion coefficient of oxygen in α -titanium is of the same order of magnitude as the diffusion coefficient in β -titanium. More recently, Roe et al. (17) have investigated diffusion of oxygen in

titanium using hardness to establish the penetration curve. Gulbransen and Andrew (18) determined diffusion in α -titanium by weight gain.

Diffusion equations as determined are:

$$\ln D_T = (-5.28) - (33,500)/RT \text{ for O in } \alpha\text{-Ti (17)}$$

$$\ln D_T = (-13.82) - (26,000)/RT \text{ for O in } \alpha\text{-Ti (18)}$$

$$\ln D_T = (+0.47) - (48,200 \pm 3,200)/RT \text{ for O in } \beta\text{-Ti (14)}$$

$$\ln D_T = (+10.35) - (68,700)/RT \text{ for O in } \beta\text{-Ti (17)}$$

$$\ln D_T = (-2.49) - (31,200 \pm 2,000)/RT \text{ for O in } \beta\text{-Ti (15)}$$

III. DIFFUSION ANALYSIS METHODS

A. Interdiffusion

The phenomenon known as diffusion is governed by a Fourier type of law which states that quantity of material, J , that flows perpendicular to a concentration gradient $\partial C/\partial x$ is proportional to a constant, D , known as the diffusion constant.

$$J = -D \frac{\partial C}{\partial x} \quad (1)$$

This formulation is known as Fick's first law. By suitable mathematical manipulation Fick's second law may be derived.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (2)$$

Depending on the boundary conditions imposed, there are several solutions of the diffusion equation in this form. From a knowledge of the penetration curve from a diffusion experiment, it is possible to determine the diffusion coefficient. Two methods are standard for the most accurate determination of diffusion coefficients.

Method I:

A diffusion couple is made between two pieces of metal. In this method it is imperative that at the end of the diffusion experiment the concentration in one half of the couple is identical after diffusion to what it was initially. This is accomplished by having one element of the couple a two-phase mixture so that the compositions of the phases remain the same during the diffusion anneal. The Van Ostrand-Dewey method or the Grube method is used for the mathematical analysis of the penetration curve obtained.

Method II:

A diffusion couple is made between two metals such that, after diffusion has occurred, the composition varies continuously from metal A to metal B. Thus, this means that the compositions that are permitted to diffuse are selected from the same single-phase field of the equilibrium diagram of the system A-B. Two techniques are commonly used for the solution of the diffusion coefficient from the penetration curve for such a method. These are (a) the Grube analysis and (b) the Boltzmann-Matano analysis. The former solution is made on the assumption that the diffusion coefficient is not a function of composition, whereas the latter takes such a variation of the diffusion coefficient into consideration. If the penetration curve is linear when plotted on probability graph paper, the diffusion coefficient is not a function of composition and then may be calculated from the slope of the rectified data. If the diffusion coefficient is a function of composition, it is determined from constructed tangents (slopes) at the various compositions.

Sketches of couple geometries for Methods I and II are presented in Figure 1.

A comprehensive knowledge of the pertinent phase diagram is a prerequisite for diffusion studies. Both the temperature range of determinations and the type of couple selected are dependent on the phase diagram. If the solid solubility is restricted, Method I is best employed. Obviously, when diffusion is occurring from a two-phase mixture, the melting temperature--or the temperature at which the mixture decomposes on heating--limits the upper temperature at which diffusion studies can be made. This may be hundreds of degrees from the melting temperature.

Method II is best employed for the determination of the diffusion coefficient when there is appreciable solid solubility. An accurate knowledge of the phase boundaries is thus necessary as a basis for the selection of the alloys from which the couple is fabricated.

Diffusion coefficients at various temperatures are related by the Arrhenius-type equation

$$D_T = D_0 e^{-Q/RT} \quad (3)$$

where D_0 is the frequency factor and Q the activation energy. This equation is linear on a $\ln D$, reciprocal temperature plot. Thus, D_0 and Q may be calculated by rectifying experimentally determined D_T values. Three or more temperature levels are required for reliability in the determination of these constants.

Penetration curves may be determined for mathematical analysis in several different ways. Basically, however, these may be classified into direct and indirect methods. The most widely used direct method is the chemical analysis of incremental portions of the interdiffused layer. Two

similar direct methods, but requiring more extensive facilities for analysis, are radioactive tracer techniques and mass-spectroscopic analysis when a stable isotope is used as a tracer. Recently, the microprobe analyzer has been used to determine directly the penetration curves of diffusion couples. Since it is not necessary to divide the diffusion couple into a finite number of increments, the latter method has the twofold advantage of being essentially a continuous penetration curve determination and permitting diffusion analyses to be made where limitations of time and temperature do not allow an extended interdiffused zone to be established.

Indirect methods such as hardness and resistivity traverses across the interdiffused layer can be used to plot the penetration curve. Inasmuch as these methods require additional experimental data to correlate the physical property with the chemical composition, they should be used only as a last resort.

B. Self-Diffusion

The most direct method of determining the self-diffusion coefficient of a metal is by analyzing a diffusion penetration curve. The diffusion couple so formed must employ an isotope of the metal to enable the penetration curve to be established. The most common method of accomplishing this is by use of a radioactive isotope and determining the penetration by autoradiographic or counting techniques. However, it is possible to use nonradioactive isotopes and to use a mass spectrometer to analyze the diffusion couple.

Attempts have been made to approximate self-diffusion phenomena by extrapolating binary diffusion data to infinite dilution. Thomas and Birchenall (19) found that this is not necessarily valid. They concluded: "The deviation of the diffusion coefficient at infinite dilution from the self-diffusion coefficient of the solvent metal is generally greater the greater the melting point depression. Both factors also tend to become greater the more limited the solid solubility of the solute metal."

Self-diffusion data have also been determined by indirect methods. Kuczynski (20, 21) has theoretically analyzed the width of the bond in sintering of fine wires and has shown that this varies as the fifth root of time. There are two objections to this method: (a) the theory is not proved; (b) reliable and reproducible data are almost impossible to obtain because of numerous other uncontrollable variables in the experimental technique.

Self-diffusion data for tungsten have been obtained by Muller (22) by observing the change of shape of a pointed wire heated in a vacuum. No independent data are available to prove this method.

The concentration at constant temperature for an identifiable atom may be expressed by

$$C = \frac{S}{2 \sqrt{\pi Dt}} \exp \left(- \frac{x^2}{4 Dt} \right) \quad (4)$$

where C is the concentration of the atom at distance x from the initial point after time t. S is the initial concentration, and D is the self-diffusion coefficient at the given temperature. This may be put in the form of the linear equation

$$\ln \left(\frac{C}{S} \right) = \ln \left(\frac{1}{2 \sqrt{\pi Dt}} \right) - \left(\frac{1}{4 Dt} \right) x^2 \quad (5)$$

The diffusion coefficient is readily solvable from the slope when the experimental data are plotted as concentration as a function of the square of distance from the surface.

From the Arrhenius equation previously discussed, the jump frequency D_0 and activation energy, Q, may be calculated from DT values determined at various temperatures.

IV. EXPERIMENTAL PROGRAM

A. Selection of Alloys for Interdiffusion Of Al, Zr, Mo, V, and O in Titanium

The research program devised for the determination of diffusion of aluminum, zirconium, molybdenum, vanadium, and oxygen in both alpha and beta titanium was the analysis of penetration curves of couples prepared by pressure welding. Couples consisted of either pure titanium with a dilute alloy of the element whose diffusion coefficient is to be determined, or of two dilute alloys of the element whose diffusion coefficient is to be determined. In the case of molybdenum, zirconium, and vanadium, it would have been possible to determine the diffusion coefficients for all compositions by forming the couple between titanium and molybdenum, zirconium, or vanadium. Such a technique is to be avoided since--as has been demonstrated by Reynolds, Averbach, and Cohen (23)--the diffusion coefficients so obtained are higher at a given alloy composition than a coefficient determined at the same alloy composition but from a couple of less severe concentration gradient. The increased diffusivity is rationalized as a result of strains associated with the concentration gradient. To minimize the effect of composition gradient strains on the diffusion coefficient, the composition gradients were kept at a minimum.

A summary of the experimental work for the determination of interdiffusion coefficients is given in Table I. In instances where there is an extended solid solubility two couples were prepared: unalloyed titanium bonded to a titanium alloy containing 5% zirconium--designated Ti/Ti-5Zr--and a bonded couple of 5 and 10% Zr alloys--designated Ti-5Zr/Ti-10Zr.

By such a technique it is possible to determine the diffusion coefficient of zirconium over a wide compositional range without undue strain effects.

It is appropriate to make a few pertinent comments with regard to the selection of the experiments listed in Table I. In general, alloying additions to commercial titanium alloys are under 10 per cent, but greater than 1 per cent. Consequently, the experimental program is designed to provide diffusion data as a function of composition up to 10 per cent.

Beta titanium is continuously soluble with zirconium, molybdenum, and vanadium. The solubility of aluminum in β -titanium is extensive. Consequently these alloys are ideally suited for diffusion couples producing a continuous penetration curve. Method II is the mathematical technique. Similarly, the solubility limits of aluminum and zirconium in alpha titanium enable these techniques to be employed.

The limited solubility of molybdenum and vanadium in alpha titanium dictate that experimental procedures and mathematical techniques of Method I be selected. It is possible that Method II could be used by fabricating a couple of titanium with a very dilute alloy (e. g., Ti/Ti-0.25Mo); however, the lack of precision with which the equilibrium diagram is known near the allotropic temperature would make it questionable whether the elements of the diffusion were in the single-phase field.

Since oxygen in titanium alloys exists principally as a contaminant, a much more restricted composition has been selected for a diffusion couple. The extended solubility of oxygen in both alpha and beta titanium enable Method II to be used.

B. Selection of Geometry for Study of Self-diffusion of Titanium

As has been previously discussed, only tracer techniques can be relied upon to give accurate self-diffusion data. For this reason, a radioactive tracer technique was selected for the determination of the self-diffusion of titanium.

Four radioactive isotopes of titanium are known. These with their respective half-lives are: Ti^{43} , 0.6 seconds; Ti^{44} , >1000 years; Ti^{45} , 3.08 hours; and Ti^{51} , 5.80 minutes. The half-lives of all but Ti^{44} are too short to enable them to be fabricated into a diffusion couple and subsequently to be annealed. Thus Ti^{44} is the only practical isotope by which diffusion experiments can be performed.

Recently, it was reported (24-26) that if scandium is bombarded with deuterons or protons in a cyclotron, a portion of the scandium is converted to Ti^{44} . This isotope has a half-life of 1000 years. The activity of the product is 10^5 disintegrations per minute. By conventional chemical techniques it is possible to separate the radioactive titanium from the scandium. However, because of the tiny amount of radioactive titanium present in the bombarded sample, microchemical techniques are necessary to prevent dilution beyond a useful radioactive level. To maximize detection sensitivity

in the determination of the self-diffusion gradient, it is imperative that the specific activity of titanium be reduced as little as possible by the addition of the non-radioactive carrier in the chemical processing.

Couples for the determination of the self-diffusion of titanium can be made by two techniques: (a) reducing Ti^{44} -enriched titanium to metallic titanium, which can be vapor-deposited on a non-radioactive titanium base, or (b) depositing Ti^{44} -enriched TiO_2 on a non-radioactive titanium surface and permitting the oxide to dissolve.

Procedure (b) is feasible since the total amount of oxygen added will be negligible or, at most, the same order of magnitude as the residual oxygen in the titanium. Inasmuch as the diffusion of oxygen is expected to be much greater than the self-diffusion of titanium, the localized concentration at the interface will be existent only for a very short time. By such a procedure the need for the microchemical reduction of a titanium salt is circumvented. A second advantage of such a procedure is that 100% of the minute quantity of radioactive titanium can be utilized by this technique as contrasted to vapor deposition.

C. Production and Analysis of Diffusion Couples

1. Preparation of Alloys

Melts weighing 150 grams were prepared in a nonconsumable electrode arc furnace. The compositions of alloys are listed as part of Table I. In instances it was necessary to make more than one alloy of a given composition so that enough stock could be prepared for the required couples. High-purity components, as shown in Table II, were used in the alloy charges.

The dilute oxygen alloy was prepared through an intermediary master alloy step. The high-purity TiO_2 was pressed and sintered at 1000°C prior to being used in preparing a 5% master alloy.

For the preparation of the self-diffusion couples, a three-pound ingot was melted.

In addition to the melts that were prepared for the manufacture of diffusion couples, a series of ten-gram ingots were melted as standards for the microprobe study. The compositions of these standards are given in Table III, along with spot chemical analysis. In all cases the chemical analyses deviate systematically from the nominal composition. Inasmuch as no weight losses were experienced in the melting, the nominal composition was subsequently used. The deviation from the nominal in the chemical analysis is attributed to the analytical method.

2. Preparation of Interdiffusion Couples

Alloys containing aluminum, zirconium, molybdenum, and vanadium were fabricated into plate $1/4$ inch thick by hot rolling at a temperature 100°C below the $\beta/\alpha + \beta$ transus. Approximately fifty minutes were accumulated in the rolling process. The rolling temperatures are tabulated as follows:

| | |
|---------|-------|
| Ti | 675°C |
| Ti-2Al | 800° |
| Ti-5Al | 825° |
| Ti-5Zr | 750° |
| Ti-10Zr | 750° |
| Ti-5V | 700° |
| Ti-10V | 650° |
| Ti-5Mo | 750° |
| Ti-7Mo | 725° |
| Ti-10Mo | 700° |

Samples 1 x 1 1/2 inches were cut from the rolled plate. These were then ground to 1/8 inch thick specimens by removing an equal amount of stock from opposite sides of the rolled plate. This scalping operation was more than sufficient to remove the contamination arising from processing in air.* The faces were then lapped to flatness by an automatic lapper. After lapping, the surfaces were thoroughly washed with petroleum ether followed by acetone. Surfaces were then etched with a solution composed of 60 cc HNO₃, 10 cc HF, 30 cc H₂O.

Roll bonding was found to be a convenient and satisfactory method to produce the bonding required for the diffusion couples. Samples to be roll bonded are encapsulated in a stainless steel container as shown in Figure 2. Prior to evacuation the container is given a very light cold reduction to prevent members of the couple from sliding out of position. The sealed unit is heated to 950°C for 15 minutes and given a one-pass 20% reduction. The capsule is then permitted to cool below 600°C and water quenched. It was subsequently established that the diffusion effect occurring during rolling was less than a detectable amount.

Several compositions could not be roll bonded until titanium sponge was introduced into the stainless steel envelope to insure complete gettering.

Specimens 5/16 inch square were sawed from the bonded plate. A total of 18 specimens was produced from the single roll-bonding operation.

The alloys containing oxygen were processed slightly differently from those described above. The ingots were rolled to slab 0.42 inch thick which was subsequently milled and lapped into plate 0.30 inch thick. Inasmuch as oxygen penetration must be determined by direct chemical analysis, the size of the interface must be larger and the planeness of the interface more accurately controlled. Roll bonding techniques did not permit a sufficiently flat interface to be produced. By hot pressing, the ripple of the interface was greatly reduced. Slabs of the alloy were canned and press bonded at 950°C with a reduction of ~32%. Eight couples, each measuring 1/2 x 3/4 inch, were cut from two bonded specimens measuring 1 1/2 x 2 inches. The variation of the interface was determined to be ~0.008 inch from photographs of the four sides of the 1/2 x 3/4 inch specimens. Diffusion minimizes the effect of the initial variation of the interface. Inasmuch as the machined layers for the penetration curve analysis were of the order of 0.015 inch thick, this initial variation is insignificant.

* This problem has been discussed by Reynolds, Ogden, and Jaffee (27).

3. Preparation of Self-diffusion Couples

The specimen designed for production of self-diffusion couples by absorption of Ti^{44} -enriched TiO_2 is shown in Figure 3. A water suspension of TiO_2 is placed in the cavity at the top and permitted to settle into an even layer at the bottom. The water is permitted to evaporate. The specimen is then heated to calcine the TiO_2 and is subsequently given the requisite diffusion anneal. After diffusion annealing, but prior to sectioning into layers, the specimen is turned to 3/8 inch diameter to eliminate effects of non-planar diffusion at the corners and to remove any irregularities due to unevenness of the precipitated TiO_2 layer at the corners.

The three-pound arc-melted ingot of titanium was forged to a one-inch round bar and subsequently machined into specimens of dimensions shown in Figure 3.

The Nuclear Science and Engineering Company of Pittsburgh, Pa., were contacted, and they agreed to undertake the production of Ti^{44} based on the literature that was supplied to them. All subsequent investigations of self-diffusion have been based on a total quantity of 0.010 grams titanium (0.016 grams TiO_2) acting as carrier for the Ti^{44} . It was decided that twelve specimens would be produced, one each for eight temperatures and four spares.

Prior to the actual production of the working self-diffusion couples, the precipitation and absorption characteristics of TiO_2 were thoroughly evaluated.

A suspension of 0.016 gram TiO_2 in a quantity of water twelve times the cavity volume of Figure 3 was prepared. The TiO_2 tended to coagulate and form a very uneven deposit on settling. If, however, a tiny amount of Alconox (a commercial wetting agent) is added, a smooth, even deposit can be produced on settling. By serial dilution experiments it was established that an 0.02% solution of Alconox was the minimum amount that was necessary to obtain the type of deposit desired.

Using an 0.02% solution of Alconox, the absorption characteristics of TiO_2 were investigated at 600°, 800°, 900°, and 1000°C. Complete absorption of the oxide was obtained under the following conditions:

| | |
|--------|--------------|
| 1000°C | 1 hr |
| 900°C | 10 hr |
| 800°C | 83 hr |
| 600°C | undetermined |

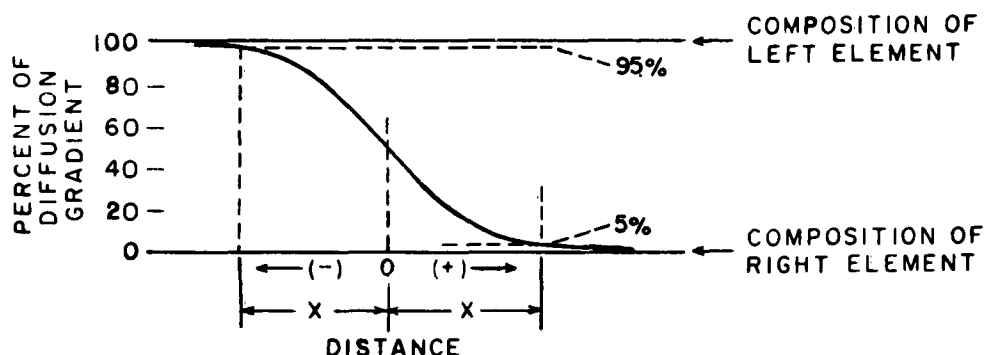
Similar absorption experiments were carried out for oxide suspensions that contained no Alconox wetting agent; the times required to dissolve the oxide were the same as above.

Details of the chemical methods used by the Nuclear Science and Engineering Corporation for the production of Ti^{44} -enriched TiO_2 are included in Appendix I.

4. Diffusion Annealing

Data contained in the review by Peterson (3) was used as a basis for the selection of annealing times at the various temperatures.

From published values of diffusion coefficients and activation energies, Grube-type calculations were made to determine the approximate width of the interdiffused zone. At constant temperature such a mathematical treatment yields solutions in the form of $x^2 = Kt$ where x is the distance from the mean composition (approximately the initial interface) and t is diffusion time. Thus a family of straight lines ($\log x$ vs $\log t$) can be constructed with temperature as a parameter. In making these calculations the distance x was made to correspond to the composition of 5% dilution from the initial composition of the element of the couple.



For a diffusion experiment where the elements of the diffusion couple are of compositions in the same phase field, a distance $2x$ corresponds to the interdiffused zone from 5% to 95% of the compositional difference of the elements of the couple. For diffusion experiments in which the composition of one element is unchanged, x corresponds to 90% of the penetration.

From such calculations times were selected so that the distance x corresponded to 1 mm, a practical penetration distance. The annealing times selected on such a basis are given in Table IV. For the interdiffusion studies, a maximum time of one month (720 hr) was imposed, and for the oxygen diffusion study a maximum diffusion time of 1000 hr was imposed.

There was no established basis for selection of diffusion times for the self-diffusion study. Since self-diffusion was expected to be considerably slower than interdiffusion, longer times than for interdiffusion were selected. Diffusion times of two months at 600°, 700°, 800°, and 900°C, and one month at 1000°, 1100°, 1200°, and 1250°C. Subsequently self-diffusion specimens were annealed for 24 hr at 1200°C and for 3 hr at 1300°C.

5. Penetration Curve Analysis for Substitutional Solutes

The diffusion experiments of the substitutional solute elements aluminum, molybdenum, vanadium, and zirconium were devised for the penetration curve analysis by electron microprobe analysis. Such a device bombards a metal specimen with a small beam of electrons ~ 0.001 mm in diameter. The scattered electrons and the characteristic X-radiation excited in the specimen are then analyzed. The Cambridge model microprobe analyzer at Armour Research Foundation has provision for deflection of the electron beam so that the distribution of elements in a small area (~ 0.3 mm square) can be displayed on cathode ray tubes.

A block diagram of the Foundation's microprobe analyzer is shown in Figure 4. Two recent publications (28, 29) by Foundation staff members give further details of its operation and outline typical metallurgical applications.

Prior to microprobe analysis, diffusion specimens had to be prepared carefully by metallographic techniques. The $5/16$ inch square specimens were hand ground to fit into the $1/4$ inch diameter specimen holder of the microprobe stage. The specimens were then mounted in Bakelite and given a metallurgical polish. Extreme care was observed that the polished surface was perpendicular to the interface. The flat sides of the specimens were used as a reference plane to maintain this perpendicularity. The specimen was broken out of the mount prior to microprobe measurements.

Microprobe specimens cannot be etched since the concentration at the plane of measurement is altered by such etching. The diffusion specimen must be positioned accurately on the microprobe stage so that solute concentration perpendicular to the interface can be determined. Since the interface could not be observed microscopically, accurate positioning was initially a problem. This difficulty was overcome by scribing a line perpendicular to the diffusion interface. The specimen was aligned on a microhardness tester and the line scribed by moving the microhardness stage under a suitable diamond.

Since the maximum deflection of the microprobe beam is ~ 0.3 mm, it was necessary to reposition the specimen on the stage of the microprobe analyzer in order to determine the complete penetration curve. To facilitate the repositioning of the specimen a series of Knoop hardness impressions were made parallel to the scribed line with the point of the Knoop impression perpendicular to the scribed line. The distance between these fiducial marks could be measured accurately with the microprobe as the scribed line and Knoop hardness impressions can be readily observed on the scattered electron image.

It was initially thought that the most expedient method of determining the penetration curves on the electron microprobe analyzer would be to drive the electron beam slowly across the interdiffused zone, measuring the concentration either photographically or by counting techniques. The electronic circuits of the instrument were modified to provide such a drive. Such a method was found to be impractical since the integrated time over a small

area was too small to eliminate the statistical counting errors. Consequently, the beam was positioned over a desired area and the concentration determined by counting for 100 seconds. The beam was then deflected to another area, and again the concentration was determined by counting for 100 seconds.

Three reference specimens were incorporated in the microprobe vacuum chamber--pure titanium and two standard specimens (see Table III) which had been water-quenched from the β -field. From these data the penetration curve, as determined in counts, could be transcribed to composition. The slight degree of nonlinearity of counts as a function of composition is therefore compensated.

The calculated composition sometimes deviated from the known composition of the elements of the couple. The penetration curve as determined by the microprobe was considered to represent diffusion from the boundary alloy conditions in the prepared couples. All subsequent calculations were made on such an assumption.

Because of the high absorption of aluminum K_{α} radiation by titanium, it is not possible to use the microprobe analyzer for diffusion studies of aluminum in titanium. It was impractical to determine the penetration curve of the aluminum diffusion samples by chemical analysis because the sample size was too small, having been selected for the microprobe technique. Attempts were made to determine the penetration curve by microprobe analysis of titanium radiation and by microhardness traverses. These attempts were unsatisfactory.

The diffused zone for molybdenum and vanadium in α -titanium was extremely narrow, making the establishment of the penetration curve subject to considerable error. Because of the extremely narrow penetration zone the solubility limits of molybdenum and vanadium could not be read from the penetration curve. A search of constitutional literature indicated that these limits are not known precisely. Inasmuch as it was necessary to know these limits to solve the diffusion equation, these had to be approximated based on the best literature data and consistent with the observed penetration curves.

Typical penetration curves are given in Figures 5 and 6 for the diffusion of vanadium in α - and β -Ti, respectively. The rectification of these and other data have been by probability-distance curves as is shown in Figures 8a and 8b for zirconium, Figures 9a and 9b for molybdenum, and Figures 10a and 10b for vanadium.

The linearity of the probability plots indicate that the diffusion coefficient is not a function of composition for the composition range investigated.

The mathematical solution of the diffusion equation may be expressed by:

$$2 \left(\frac{c - c_0}{c_i - c_0} \right) - 1 = \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (6)$$

where $(c_i - c_0)$ is the diffusion gradient, c the composition at point x , measured from the position where the error function (erf) is 50%; c_0 and c_i are the

boundary compositions of the diffusion couple. A typical solution of the diffusion coefficient from rectified data is given in Appendix II. Deviations from linearity of data at the extremes of probability plots according to the work of Johnson (30) are a result of inaccuracies of the chemical analyses and consequently should be ignored in constructing the best straight-line fit prior to making the mathematical calculation of the diffusion coefficient.

Calculated diffusion coefficients are summarized in Table V. The logarithms of these coefficients were then plotted as a function of reciprocal temperature (Figs. 12 and 13) from which least-squares solutions were made. For systems where the diffusion coefficients were determined at three or more temperatures, the standard errors in $\ln D_0$ and Q were calculated by standard statistical analysis methods.

$$\ln D_T = (-27.14 \pm 1.56) - (11,800 \pm 3,000)/RT \text{ for Zr in } \alpha\text{-Ti}$$

$$\ln D_T = (-4.01 \pm 1.22) - (40,100 \pm 3,300)/RT \text{ for Zr in } \beta\text{-Ti}$$

$$\ln D_T = (-17.19) - (28,400)/RT \text{ for Mo in } \alpha\text{-Ti}$$

$$\ln D_T = (-9.00 \pm 0.92) - (33,100 \pm 2,400)/RT \text{ for Mo in } \beta\text{-Ti}$$

$$\ln D_T = (-31.39) - (3,100)/RT \text{ for V in } \alpha\text{-Ti}$$

$$\ln D_T = (-4.38 \pm 1.04) - (41,400 \pm 2,800)/RT \text{ for V in } \beta\text{-Ti}$$

6. Penetration Curve Analysis for Oxygen Diffusion

Penetration curves for the diffusion of oxygen in titanium were determined by vacuum fusion analysis of machined layers of diffusion couples.

The Ti-O diffusion couples were machined into layers by end milling. A specially designed fixture permitted collection of all machined chips without contamination. The thickness of the machined layer was calculated by the difference in height from the reference surface. For specimens annealed 900°-1300°C, layers 0.015 inch were machined; at the lower temperatures 0.015 inch cuts were made up to where the interface was, 0.005 inch cuts through the diffused zone for 700° and 800°C specimens, and 0.003 inch cuts for the 600°C specimen. Alternate layers were analyzed by vacuum fusion analysis. Prior to analysis, the machined chips were carefully washed with acetone.

The penetration curves showed the classical shape--for the most part, being smooth curves with a minimum of fluctuation. However, the end values were at considerable variance from the nominal, unalloyed titanium and Ti-0.5 wt % O. The analyzed compositions of the elements were subsequently determined: 0.0229% and 0.394% oxygen in the as-bonded condition, and 0.0289% and 0.400% in the as-melted and rolled state.

It was initially thought that the increase in oxygen after diffusion annealing was attributable to contamination on the surface. Consequently, a 0.030 inch layer was machined from the sides prior to machining into layers. Except at the lower temperatures this removal had no appreciable effect on the analysis since, for the diffusion times required, the contamination diffuses almost completely through the specimen.

Terminal compositions as established by the penetration curves varied from the original composition limits. Since this variation was more pronounced at the elevated temperatures, there can be no question but that this is attributable to contamination during annealing. In making the mathematical analysis, it is assumed that the limits of the penetration curve as analyzed represent diffusion between the limits of the original composition, 0.03 and 0.40 wt % O, respectively.

The mathematical solution and analysis of diffusion data for the dilute oxygen alloys is identical to that presented in the previous section. A typical penetration curve for oxygen is given in Figure 7. Probability-distance plots of the penetration data are shown in Figs. 11 a and 11 b which yield diffusion coefficients summarized in Table V. By fitting these data to the Arrhenius equation the following equations were obtained by least-squares solutions and subsequent statistical analysis for the errors:

$$\ln D_T = (-14.94 \pm 1.15) - (16,200 \pm 2,200)/RT \text{ for O in } \alpha\text{-Ti}$$

$$\ln D_T = (+8.37 \pm 2.21) - (66,800 \pm 7,000)/RT \text{ for O in } \beta\text{-Ti}$$

7. Penetration Curves for Self-diffusion

The month-long anneals at temperatures above 1000°C were impractical for several reasons. First of all, at 1200° and 1250°C the quartz capsules devitrified resulting in deterioration of the specimen by oxidation. The specimens annealed at 1000° and 1100°C for one month deformed during annealing by grain growth, distorting the planar geometry established for the diffusion experiment. Finally, as was established on subsequent analysis, the time of annealing was far too long to permit a satisfactory gradient by which to calculate the diffusion coefficient.

As indicated by equations 6 and 7, machined layers must be taken at known distances from the interface. The device used for machining the Ti-O diffusion couples was satisfactorily employed in the preparation of machined layers of the self-diffusion couples. All measurements were made from the bottom surface as a reference plane. Layers were machined according to the following schedule: 0.000 (surface) to 0.005 inch into 0.001 inch thick increments; 0.005 to 0.035 inch into 0.002 inch thick increments for specimens annealed at 900°-1300°C; and 0.005 to 0.025 inch into 0.002 inch thick increments for specimens annealed at 600°-800°C. There was no need to wash the machined chips since any slight oil contamination would not affect the radioactivity analysis. The machining equipment, however, was meticulously cleaned between incremental cuts to prevent carryover of radioactive chips. The weight of the machined chips was carefully measured on a precision balance.

The decay scheme of Ti^{44} has been described by Cybulska and Marquay (31), as shown in Fig. 14.

The activity of Ti^{44} was measured by counting in a well-type NaCl (Tl) crystal 1 3/4 inch diam. x 2 inches with a 3/4 inch diam., 1 inch deep well. The crystal was contained in a low-background shielding system.

The titanium chips were contained in cellulose nitrate test tubes. The counter used was a Nuclear Data Corporation Model ND 130, 512 channel pulse height analyzer.

Two sets of data were obtained. First, by setting the lower discriminator to a low value the activity of both $Ti^{44} \rightarrow Sc^{44}$ and $Sc^{44} \rightarrow Ca^{44}$ were obtained. Secondly, by setting the discriminator to approximately 150 kev, only the $Sc^{44} \rightarrow Ca^{44}$ activity was obtained. These measurements were proportional. The former was used in plotting the penetration curves. Background measurements were taken for correction purposes. Activity was measured for at least one minute, or for a sufficient time interval for over 10,000 counts. In some instances, counting times up to one hour were necessary. Because of the intensity of the activity, the error due to counting is extremely small--from less than 1% for the great bulk of the readings to approximately 3% for some of the very weak activity measurements. Weighing and distance measurement errors are by far the prime source of error in establishing the penetration curve.

The specific activity is obtained by dividing the activity rate by the weight of the specimen. Penetration curves for the self-diffusion of titanium are presented in Figs. 15a-15g for 600°, 700°, 800°, 900°, 1000°, 1200°, and 1300°C. Only those curves at 600°, 700°, 800°, 1200°, and 1300°C are amenable to diffusion calculations. The calculated diffusion coefficients are summarized in Table VI.

The diffusion coefficients have been plotted as log D-reciprocal temperature in Fig. 16. From this it is at once seen that the diffusion coefficient at 600°C is non-consistent with the data of 700° and 800°C. The datum at 600° was not used in making the frequency factor D_0 and activation energy calculations.

The self-diffusion data permit the following equations to be evaluated:

$$\ln D_T = (-21.08) - (5,700)/RT \text{ for } \alpha\text{-Ti}$$

$$\ln D_T = (-8.40) - (28,600)/RT \text{ for } \beta\text{-Ti}$$

V. DISCUSSION

The use of the electron microprobe analyzer has proved to be an excellent and most reliable tool in the determination of interdiffusion gradients. However, even such a facile tool has limitations as was found in the case of the detection of interdiffusion of aluminum in titanium. The use of such an instrument enables the accurate delineation of a diffusion gradient that could not be done by conventional chemical analysis techniques. There was no previous experience of prior workers on which to draw in planning the experiments for the microprobe analysis. With one exception the techniques developed were very good; it is recommended that means be incorporated in the sample to identify the original interface. Tungsten wires or thoria powder would be expected to serve extremely well as such means.

The calculation of diffusion constants for oxygen in titanium presented in this investigation is the first instance in which the fundamental diffusion geometry was used and penetration curves established by direct chemical analysis. The diffusion data for oxygen in both α - and β -titanium were classical; the penetration curves were smooth with a minimum amount of deviation. The diffusion coefficients were consistent with the Arrhenius relationship. The minor contamination some specimens experienced at the high annealing temperatures should not have affected the results deleteriously.

The present investigation represents the first use of a radioactive isotope of titanium in metallurgical research. It is unfortunate that the annealing times chosen were too long to enable significant constants to be calculated at most temperatures. However, the data so obtained in this investigation tend to support observations made by Kidson and McGurn (10) for zirconium that the activation energy for self-diffusion determined directly can be much lower than that determined by indirect means.

The jump frequency, D_0 , and the activation energy, Q , of the diffusion equation

$$D_T = D_0 e^{-Q/RT}$$

must be solved from data obtained at several temperatures. A maximum of five data were available for a statistical analysis of the errors of the constants of β -titanium; a maximum of three for α -titanium. This certainly is not ideal for a precise determination of the diffusion constants. Ideally, multiple determinations should be made at temperatures at 25° or 50°C intervals rather than single determinations at 100°C intervals as was necessary by the broad scope of the present investigation.

The standard errors associated with Arrhenius equation are in Q and $\ln D_0$. It is therefore difficult to express meaningfully the temperature dependence of the diffusion coefficient with the associated errors in any other than the logarithmic form. The logarithmic form was consequently used throughout this report.

The errors of the constants of the Arrhenius equation vary widely but, in general, are better for diffusion in β - rather than α -titanium. With the exception of molybdenum, the activation energies are within 10% for β -titanium; the errors in $\ln D_0$ are up to 30%. For α -titanium (in the two systems that permitted statistical analysis) the error in $\ln D_0$ was less than 10%, but the error in Q was as great as 25%. These observations point to the great need for multiple data if precise diffusion data are desired. Due caution must also be observed in the casual use of published diffusion data to which no error limits have been affixed.

The diffusion equations determined in this investigation may be compared with those of Goold (12) for molybdenum and vanadium in β -titanium, and with Roe et al. (17) for oxygen in β -titanium:

$$\ln D_T = (-9.00 \pm 0.92) - (33,100 \pm 2,400)/RT \text{ for Mo in } \beta\text{-Ti} \quad (\text{this report})$$

$$\ln D_T = (-11.51) - (21,900)/RT \text{ for Mo in } \beta\text{-Ti} \quad (\text{Ref. 12})$$

$$\ln D_T = (-4.38 \pm 1.04) - (41,400 \pm 2,800)/RT \text{ for V in } \beta\text{-Ti} \quad (\text{this report})$$

$$\ln D_T = (-5.12) - (39,600)/RT \text{ for V in } \beta\text{-Ti} \quad (\text{Ref. 12})$$

$$\ln D_T = (+8.37 \pm 2.21) - (66,800 \pm 7,000)/RT \text{ for O in } \beta\text{-Ti} \quad (\text{this report})$$

$$\ln D_T = (+10.35) - (68,700)/RT \text{ for O in } \beta\text{-Ti} \quad (\text{Ref. 17})$$

The agreement of the data above with published data is indicative of the over-all quality of the data in the present investigation as limited by the number of determinations from which the constants in the diffusion equation were calculated.

Several comments are pertinent with respect to the magnitude of the constants for the diffusion equation calculated in this investigation:

(a) The values of D_0 for interdiffusion of zirconium and vanadium in α -titanium are several orders of magnitude smaller than generally observed for refractory metals. It can well be argued that the relatively short diffusion time prevented accurate data from being established for molybdenum, but such is not the case for zirconium. In diffusion couples of the latter element in titanium smooth penetration curves were observed yielding diffusion coefficients in accord with the Arrhenius equation. The low value of D_0 for zirconium adds credence to the preliminary data for vanadium. The observation is worthy of further study from a mechanistic standpoint.

(b) LeClaire (32) suggests that D_0 for self-diffusion varies from 0.1 to 10 ($\ln D_0$ from -2.3 to +2.3). On this basis of standard, the preliminary calculations of D_0 for the self-diffusion of titanium are small. Data for self-diffusion of refractory alloys summarized by Peterson (3) tend to support this observation; however, an extreme from $D_0 = 6.3 \cdot 10^7$ ($\ln D_0 = 18.0$) for tungsten to $D_0 = 10^{-4}$ ($\ln D_0 = -9.2$) for chromium are also recorded by Peterson. From the literature data for other self-diffusion constants it appears that the calculated value for D_0 for self-diffusion of titanium is too small, although this can be ascertained with certainty after further determinations.

On the basis of the investigations conducted the following recommendations are made:

(a) The methods that have been developed for the determination of self-diffusion in titanium give every evidence of being practical. A redetermination of the self-diffusion of titanium is certainly justified.

(b) The interdiffusion of molybdenum and vanadium in α -titanium should be redetermined by employing diffusion anneals of at least six months and with some inert marker at the interface.

(c) The accuracy of the diffusion constants of the alloying elements in β -titanium and for oxygen and zirconium in α -titanium as calculated in this investigation was limited by the number of evaluations of diffusion coefficients and temperatures employed. If the calculated values of Q and D_0 are to be refined, it will be necessary to use a statistical approach through the use of a far greater number of individual diffusion couples.

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TABLE I
SUMMARY OF INTERDIFFUSION STUDIES

| System | α or β Ti | Maximum Solubility in Ti, wt % | Composition of Couple | Temperatures, °C | Analytical Technique for Penetration Determination | Mathematical Technique* |
|--------|------------------------|--------------------------------|---|-------------------------------|--|-------------------------|
| Ti-Al | α | 25 | $\left\{ \begin{array}{l} \text{Ti/Ti-2Al} \\ \text{Ti/Ti-5Al} \end{array} \right\}$ | 600, 700, 800 | Microprobe | II |
| | β | 30 | $\left\{ \begin{array}{l} \text{Ti/Ti-2Al} \\ \text{Ti/Ti-5Al} \end{array} \right\}$ | 900, 1000, 1100 1200, 1300 | Microprobe | II |
| Ti-Zr | α | 100 | $\left\{ \begin{array}{l} \text{Ti/Ti-5Zr} \\ \text{Ti-5Zr/Ti-10Zr} \end{array} \right\}$ | 600, 700, 800 | Microprobe | II |
| | β | 100 | $\left\{ \begin{array}{l} \text{Ti/Ti-5Zr} \\ \text{Ti-5Zr/Ti-10Zr} \end{array} \right\}$ | 900, 1000, 1100 1200, 1300 | Microprobe | II |
| Ti-Mo | α | ~1 | $\left\{ \begin{array}{l} \text{Ti/Ti-7Mo} \\ \text{Ti/Ti-5Mo} \end{array} \right\}$ | 600, 700, 800 | Microprobe | I |
| | β | 100 | $\left\{ \begin{array}{l} \text{Ti/Ti-5Mo} \\ \text{Ti-5Mo/Ti-10Mo} \end{array} \right\}$ | 900, 1000, 1100 1200, 1300 | Microprobe | II |
| Ti-V | α | 1-2 | $\left\{ \begin{array}{l} \text{Ti/Ti-10V} \\ \text{Ti/Ti-5V} \end{array} \right\}$ | 600, 700 | Microprobe | I |
| | α | 1-2 | $\left\{ \begin{array}{l} \text{Ti/Ti-5V} \\ \text{Ti/Ti-10V} \end{array} \right\}$ | 800 | Microprobe | I |
| | β | 100 | $\left\{ \begin{array}{l} \text{Ti/Ti-5V} \\ \text{Ti-5V/Ti-10V} \end{array} \right\}$ | 900, 1000, 1100 1200, 1300 | Microprobe | II |
| Ti-O | α | 14 | $\left\{ \begin{array}{l} \text{Ti/Ti-0.5O} \\ \text{Ti/Ti-0.5O} \end{array} \right\}$ | 600, 700, 800 | Vacuum fusion | II |
| | β | 4 | | 1000, 1100, 1200 1300 | Vacuum fusion | II |

* See discussion in Section III-A of this report.

** Alloy couples in brackets are for the determination of diffusion characteristics as a function of composition.

TABLE II
MATERIALS USED IN PRODUCTION OF ALLOYS

| Material | Grade | Supplier |
|------------------|-----------------------------|---------------------------------|
| Titanium | Double-refined electrolytic | Chicago Development Corporation |
| Aluminum | 99.99% double refined | Aluminum Company of America |
| Zirconium | Iodide | Foote Mineral |
| Molybdenum | High-purity sheet | Fansteel |
| Vanadium | Electrolytic | Bureau of Mines |
| Titanium Dioxide | Specially prepared 99.9% | Bureau of Mines |

TABLE III
MICROPROBE STANDARDS

| Composition | Chemical Analysis |
|-------------|-------------------|
| Ti-1% Al | |
| 2% Al | 2.025% Al |
| 3% Al | |
| 4% Al | |
| 5% Al | 5.540% Al |
| Ti-1% V | |
| 3% V | |
| 5% V | 4.750% V |
| 7.5% V | |
| 10% V | 9.630% V |
| Ti-1% Mo | |
| 3% Mo | |
| 5% Mo | 5.45% Mo |
| 7.5% Mo | |
| 10% Mo | 10.50% Mo |
| Ti-1% Zr | |
| 3% Zr | |
| 5% Zr | 5.96% Zr* |
| 7.5% Zr | |
| 10% Zr | 11.15% Zr* |

* Single determination; others are average of duplicate determinations.

TABLE IV
SUMMARY OF ANNEALING TIMES FOR INTERDIFFUSION STUDIES

| Diffusion Couple | Diffusion Annealing Time (hr), at Temperatures | | | | | | | |
|------------------|--|-------|-------|-------|--------|--------|--------|--------|
| | 600°C | 700°C | 800°C | 900°C | 1000°C | 1100°C | 1200°C | 1300°C |
| Ti/Ti-2Al | 720 | 720 | 720 | 98 | 42 | 23 | 12 | 7.5 |
| Ti/Ti-5Al | 720 | 720 | 720 | 98 | 42 | 23 | 12 | 7.5 |
| Ti/Ti-5Zr | 720 | 720 | 720 | 520 | 140 | 44 | 16 | 4.4 |
| Ti-5Zr/Ti-10Zr | 720 | 720 | 720 | 520 | 140 | 44 | 16 | 4.4 |
| Ti/Ti-5Mo | --- | --- | --- | 420 | 190 | 92 | 48 | 28 |
| Ti/Ti-7Mo | 720 | 720 | 720 | --- | --- | --- | --- | --- |
| Ti-5Mo/Ti-10Mo | --- | --- | --- | 420 | 190 | 92 | 48 | 28 |
| Ti/Ti-5V | --- | --- | 720 | 520 | 140 | 44 | 16 | 4.4 |
| Ti/Ti-10V | 720 | 720 | --- | --- | --- | --- | --- | --- |
| Ti-5V/Ti-10V | --- | --- | --- | 520 | 140 | 44 | 16 | 4.4 |
| Ti/Ti-0.5O | 1000 | 1000 | 1000 | 900 | 135 | 48 | 14 | 4.8 |

TABLE V
SUMMARY OF CALCULATED INTERDIFFUSION COEFFICIENTS

| Temperature, °C | Diffusion Coefficient (cm ² /sec) in Titanium | | | |
|-------------------------------------|--|-----------------------|-----------------------|-----------------------|
| | Zr | Mo | V | O |
| <u>α-Titanium</u> | | | | |
| 600° | $1.69 \cdot 10^{-15}$ | $2.64 \cdot 10^{-15}$ | $3.91 \cdot 10^{-15}$ | $3.05 \cdot 10^{-11}$ |
| 700° | $4.47 \cdot 10^{-15}$ | --- (a) | $4.7 \cdot 10^{-15}$ | $6.58 \cdot 10^{-11}$ |
| 800° | $5.95 \cdot 10^{-15}$ | $2.38 \cdot 10^{-14}$ | --- (b) | $1.79 \cdot 10^{-10}$ |
| <u>β-Titanium</u> | | | | |
| 900° | $6.66 \cdot 10^{-10}$ | $8.07 \cdot 10^{-11}$ | $2.60 \cdot 10^{-10}$ | $9.26 \cdot 10^{-10}$ |
| 1000° | $1.90 \cdot 10^{-9}$ | --- (c) | $9.67 \cdot 10^{-10}$ | $1.98 \cdot 10^{-8}$ |
| 1100° | $9.97 \cdot 10^{-9}$ | $7.47 \cdot 10^{-10}$ | $2.49 \cdot 10^{-9}$ | $2.16 \cdot 10^{-7}$ |
| 1200° | $1.60 \cdot 10^{-8}$ | $1.38 \cdot 10^{-9}$ | $7.64 \cdot 10^{-9}$ | $4.41 \cdot 10^{-7}$ |
| 1300° | $5.40 \cdot 10^{-8}$ | --- (c) | $2.92 \cdot 10^{-8}$ | $1.57 \cdot 10^{-6}$ |

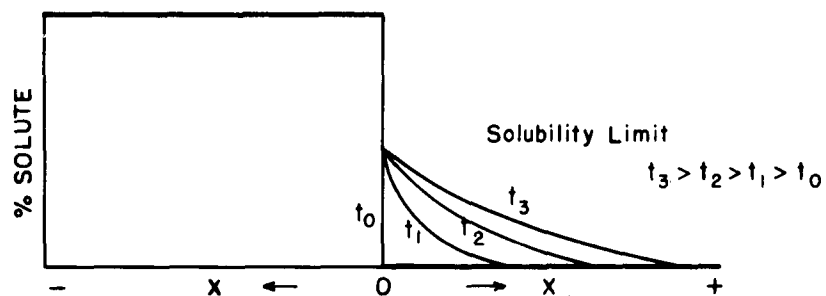
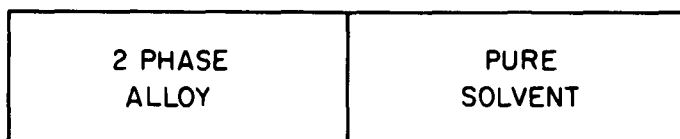
(a) No diffusion zone detected

(b) Temperature too high for boundary conditions of Method I

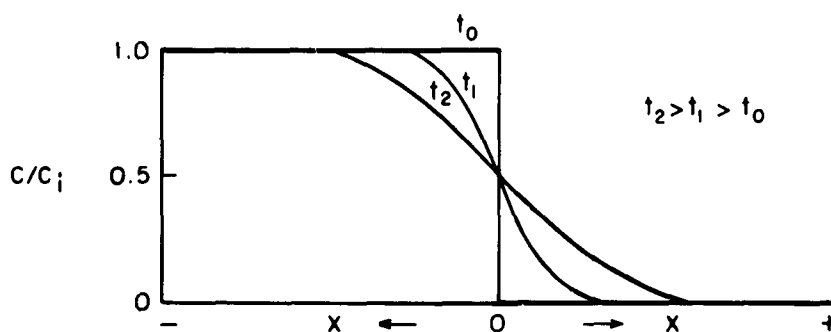
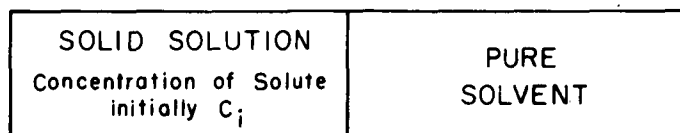
(c) Too much experimental scatter to make precise analysis

TABLE VI
SUMMARY OF CALCULATED SELF-DIFFUSION
COEFFICIENTS FOR TITANIUM

| Temperature, °C | Diffusion Coefficient, cm ² /sec |
|--------------------|--|
| <u>α-Titanium</u> | |
| 600° | $8.83 \cdot 10^{-11}$ |
| 700° | $3.16 \cdot 10^{-11}$ |
| 800° | $4.16 \cdot 10^{-11}$ |
| <u>β-Titanium</u> | |
| 1200° | $1.29 \cdot 10^{-8}$ |
| 1300° | $2.41 \cdot 10^{-8}$ |



METHOD I



METHOD II

FIG. 1 - SCHEMATIC DRAWINGS SHOWING DIFFUSION
FOR SUCCESSIVE TIMES IN METHODS I AND II

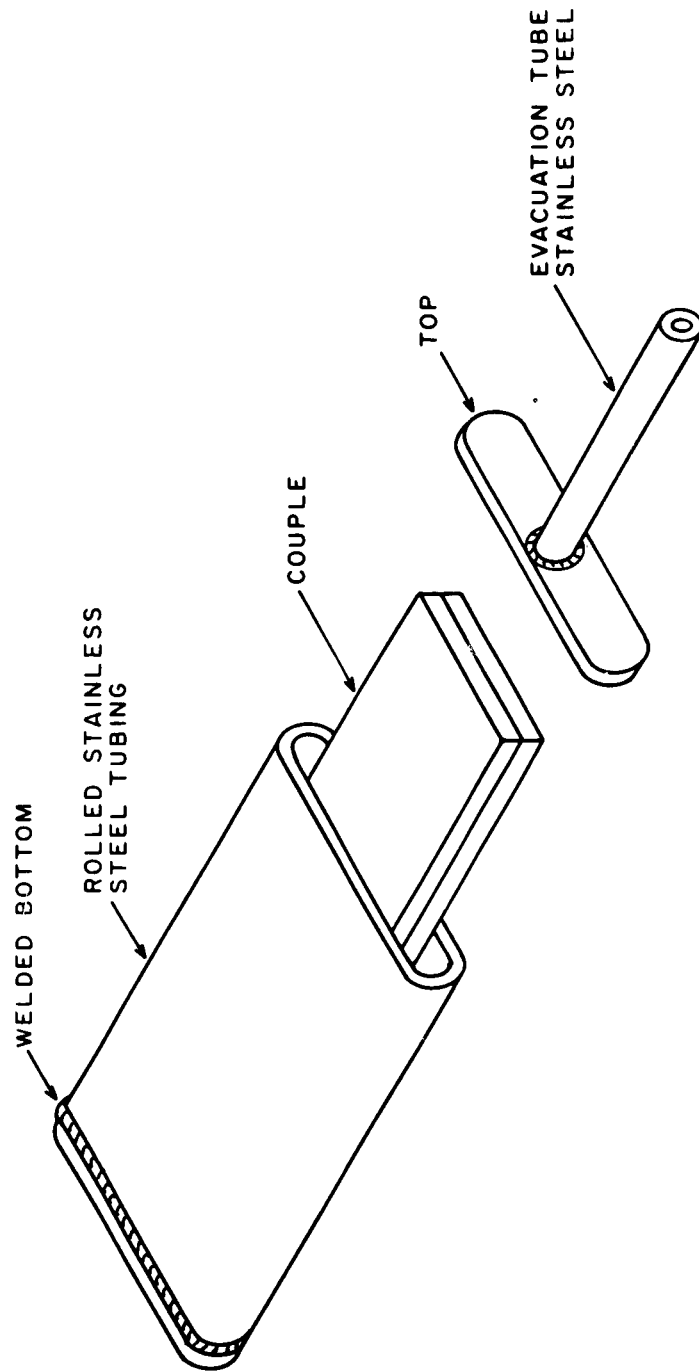


FIG. 2 - CANNING PROCESS FOR DIFFUSION COUPLES.

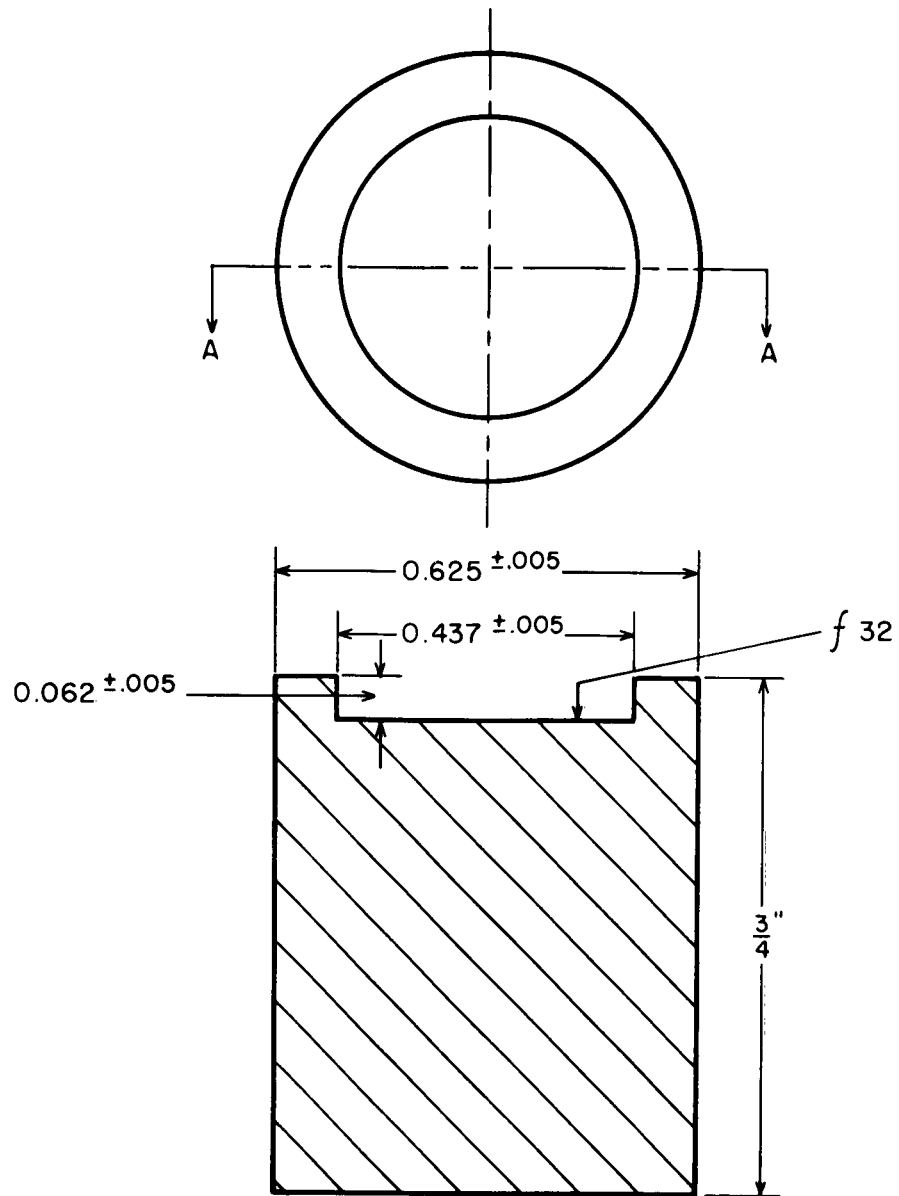


FIG. 3 - TITANIUM SPECIMEN FOR SELF-DIFFUSION STUDIES

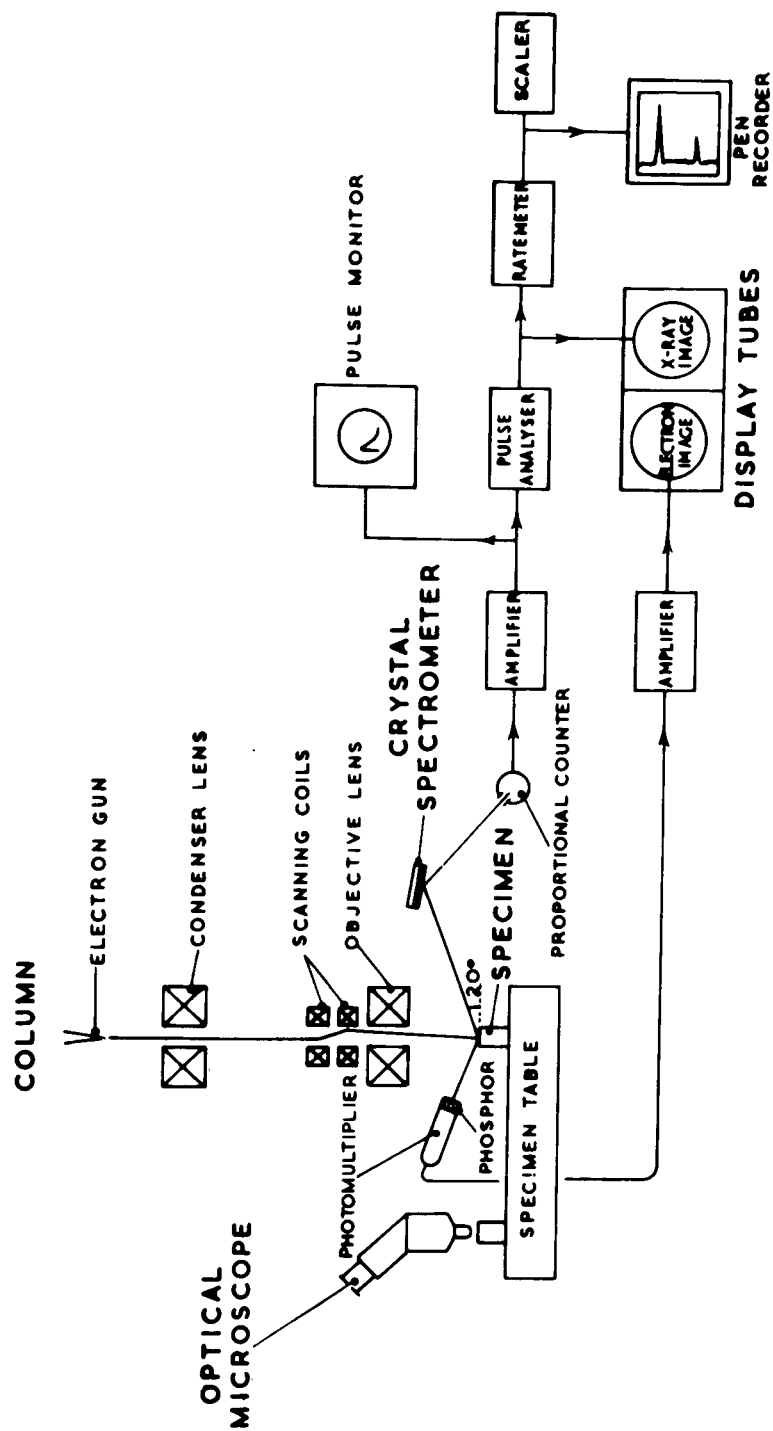


FIG. 4 - BLOCK DIAGRAM OF CAMBRIDGE INSTRUMENT
ELECTRON MICROPROBE ANALYZER.

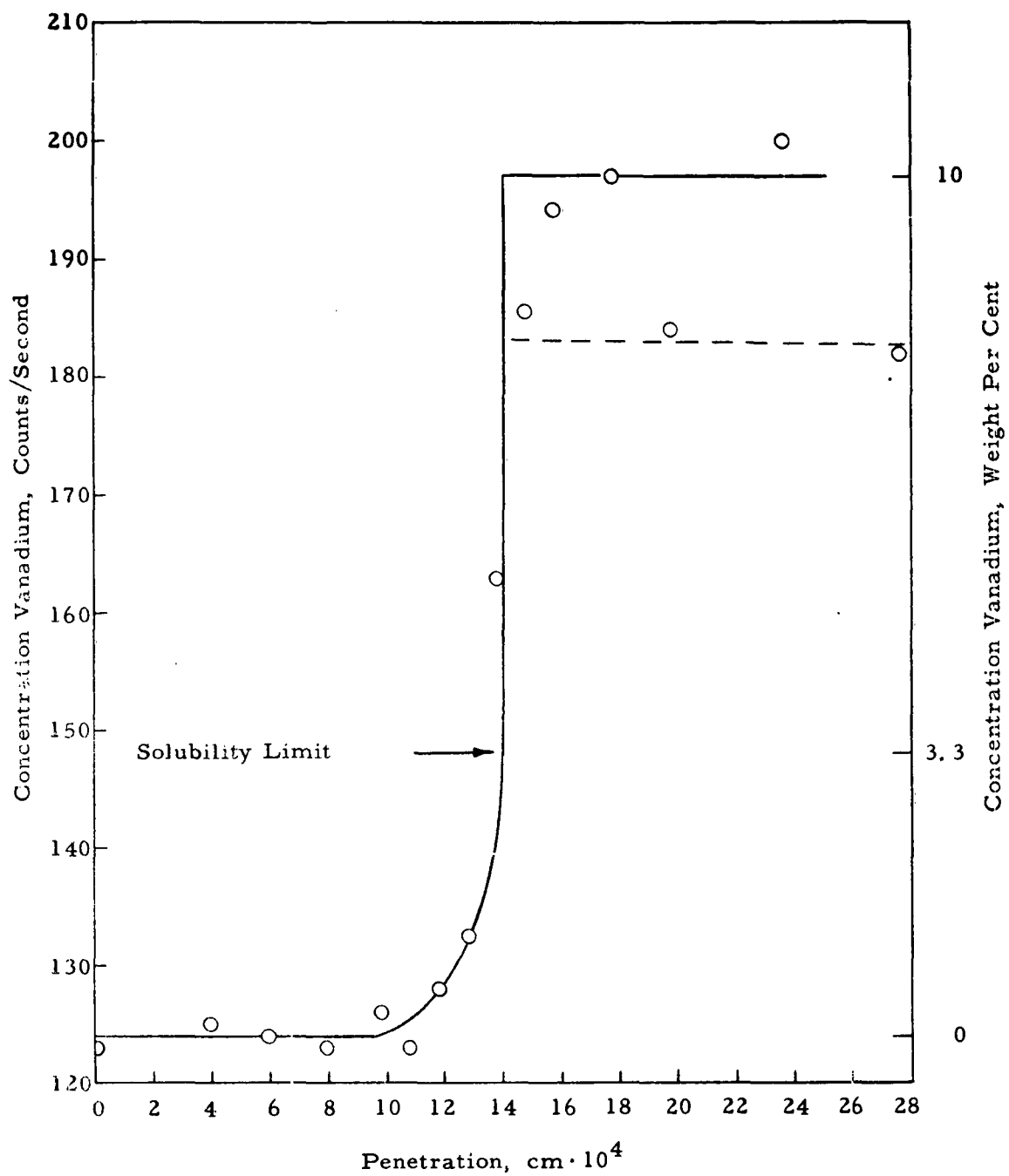


FIG. 5 - PENETRATION CURVE OF Ti/Ti-10V COUPLE
ANNEALED 720 HOURS AT 600°C.

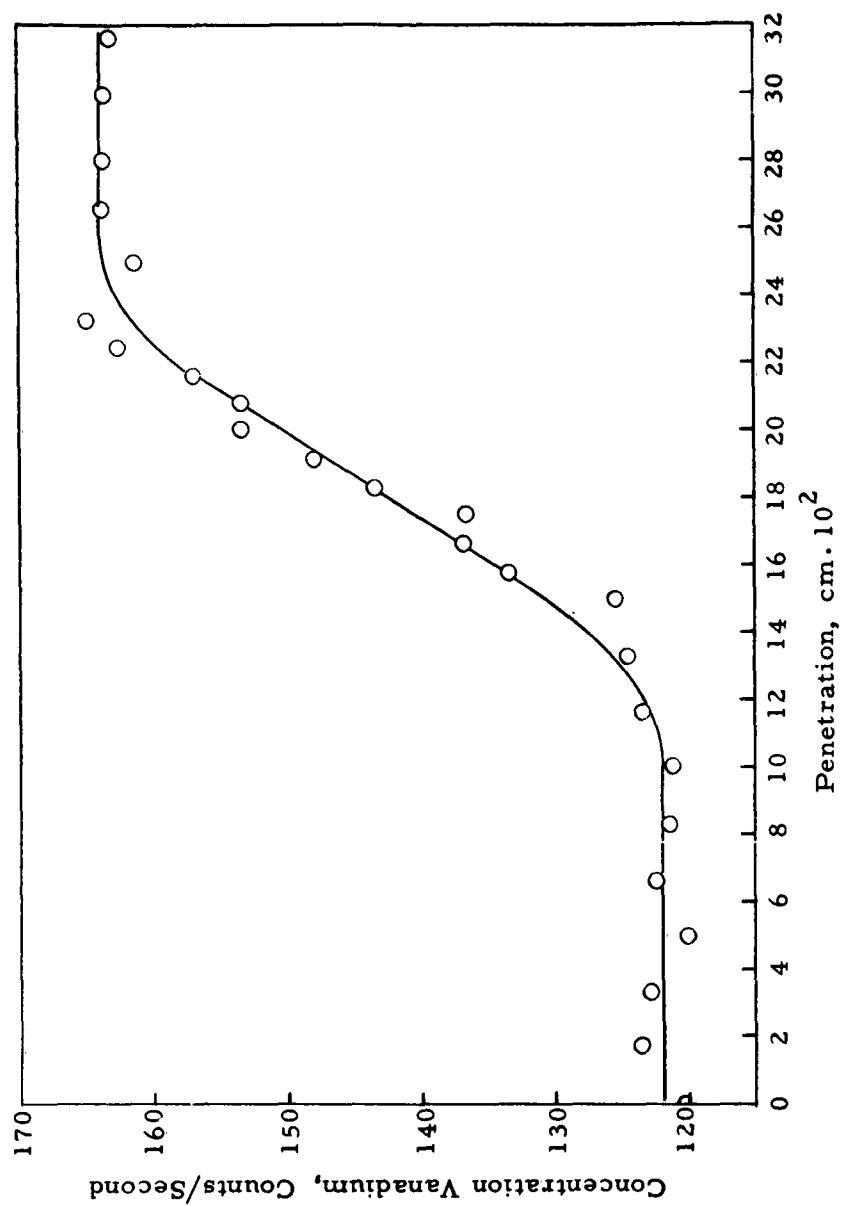


FIG. 6 - PENETRATION CURVE OF Ti/Ti-5V COUPLE ANNEALED
16 HOURS AT 1200°C.

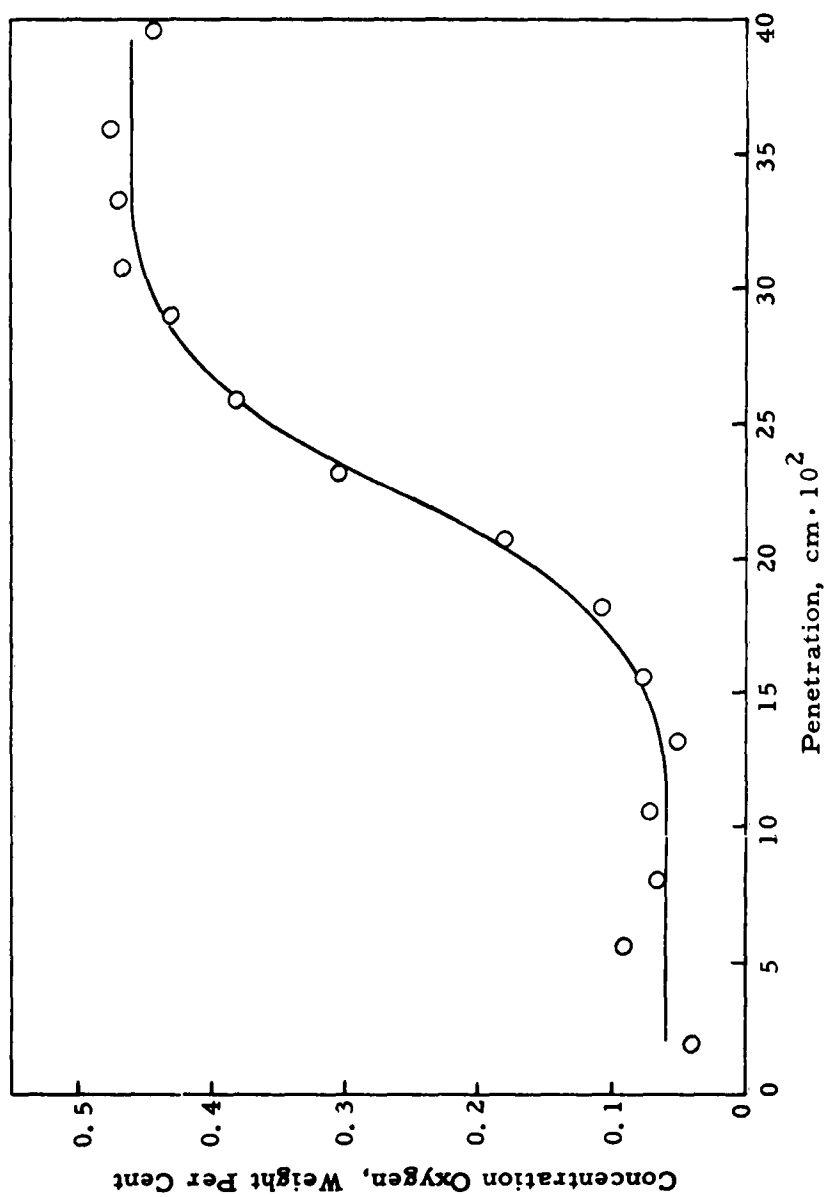


FIG. 7 - PENETRATION CURVE OF Ti/Ti-0.5 O COUPLE ANNEALED
1000 HOURS AT 800°C.

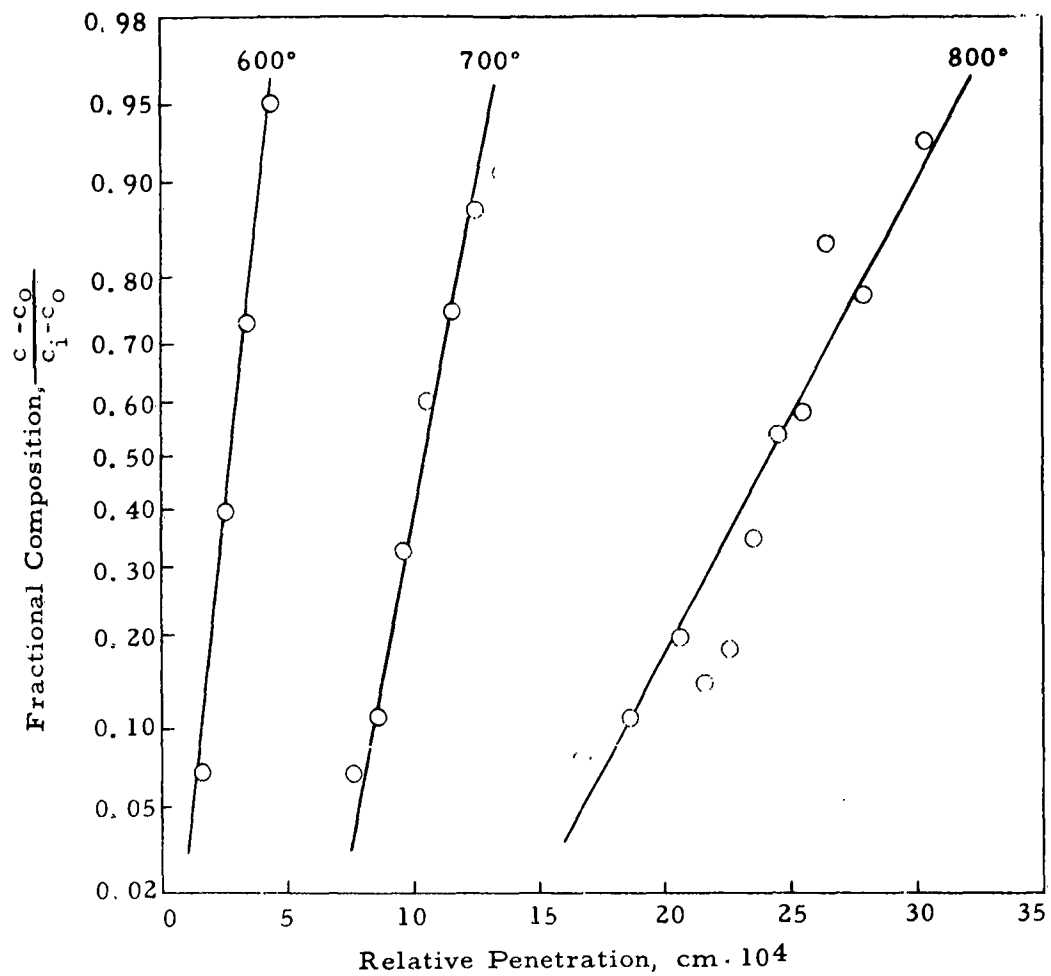


FIG. 8 a - PROBABILITY PLOTS OF Ti/Ti-5Zr COUPLES ANNEALED AT 600°, 700°, AND 800°C FOR 720 HOURS.

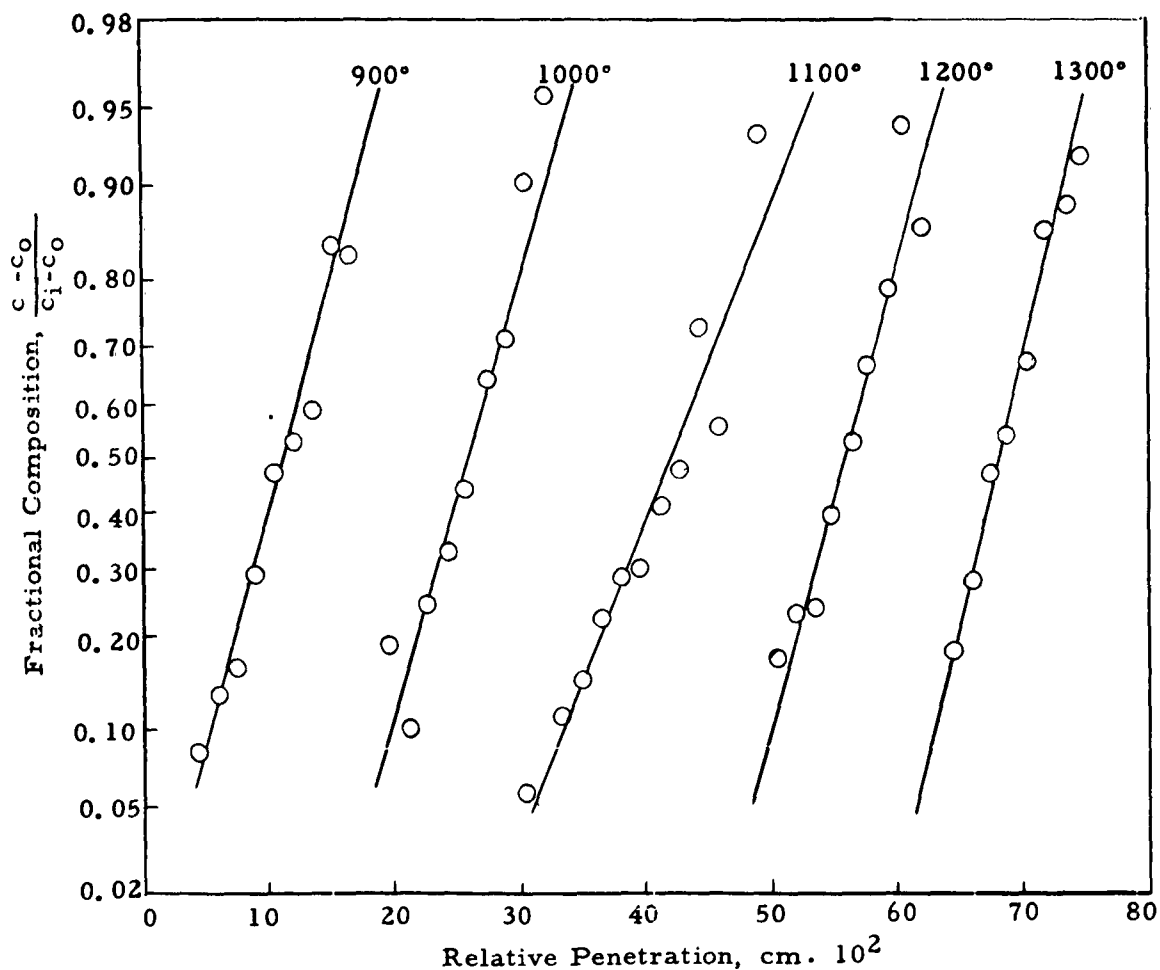


FIG. 8b - PROBABILITY PLOTS OF Ti/Ti-5Zr COUPLES ANNEALED AT 900°, 1000°, 1200°, AND 1300°C FOR 520, 140, 44, 16, AND 4.4 HOURS, RESPECTIVELY.

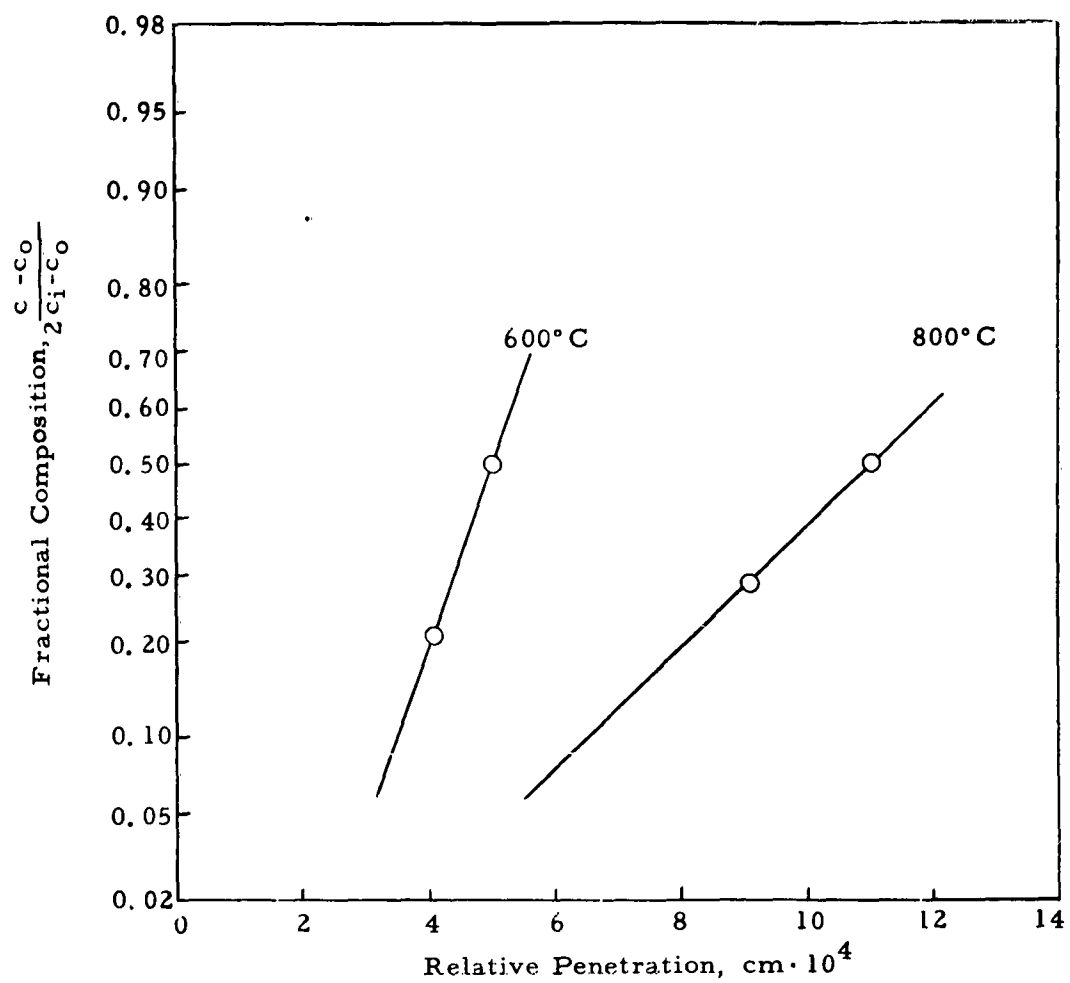


FIG 9a - PROBABILITY PLOTS OF Ti/Ti-7Mo COUPLES
ANNEALED AT 600° AND 800°C FOR 720 HOURS.

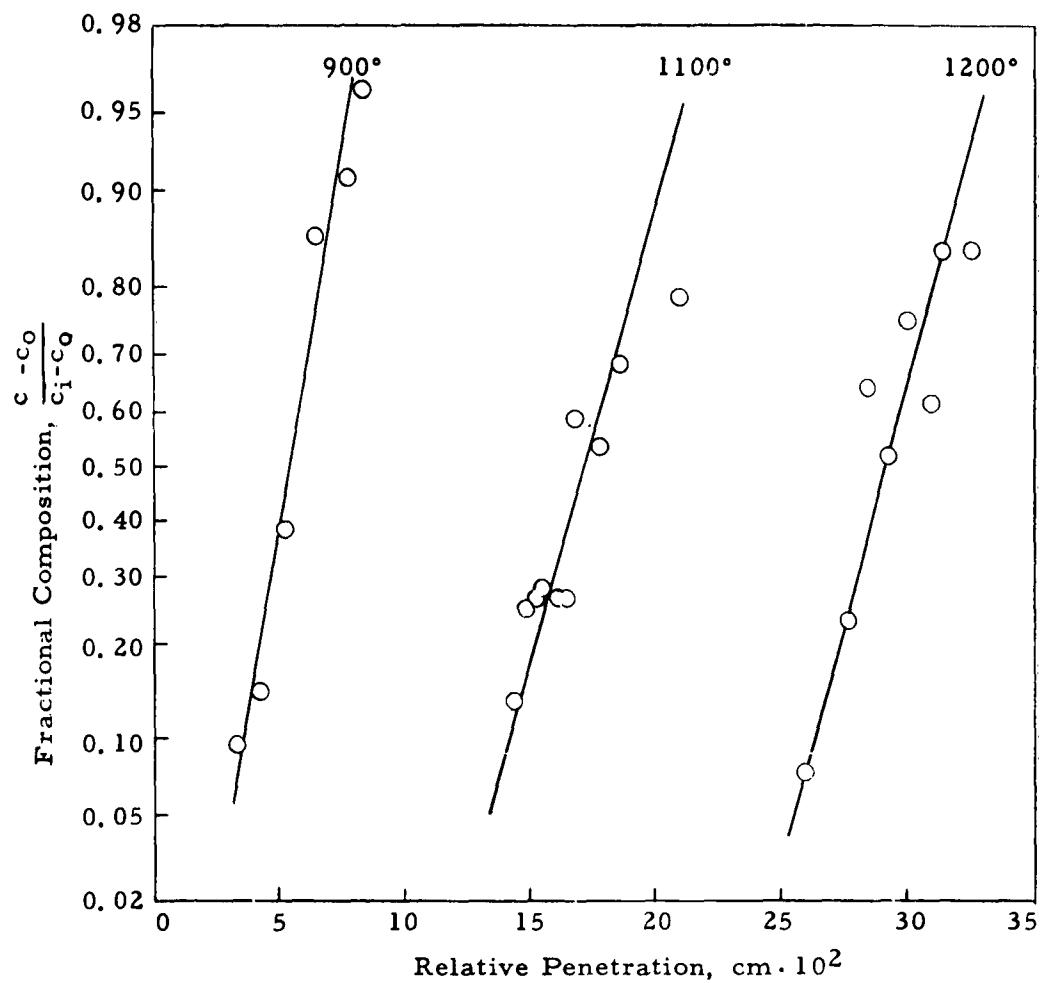


FIG. 9b - PROBABILITY PLOTS OF Ti/Ti-5Mo COUPLES ANNEALED AT 900°, 1100°, AND 1200°C FOR 420, 92, AND 48 HOURS, RESPECTIVELY.

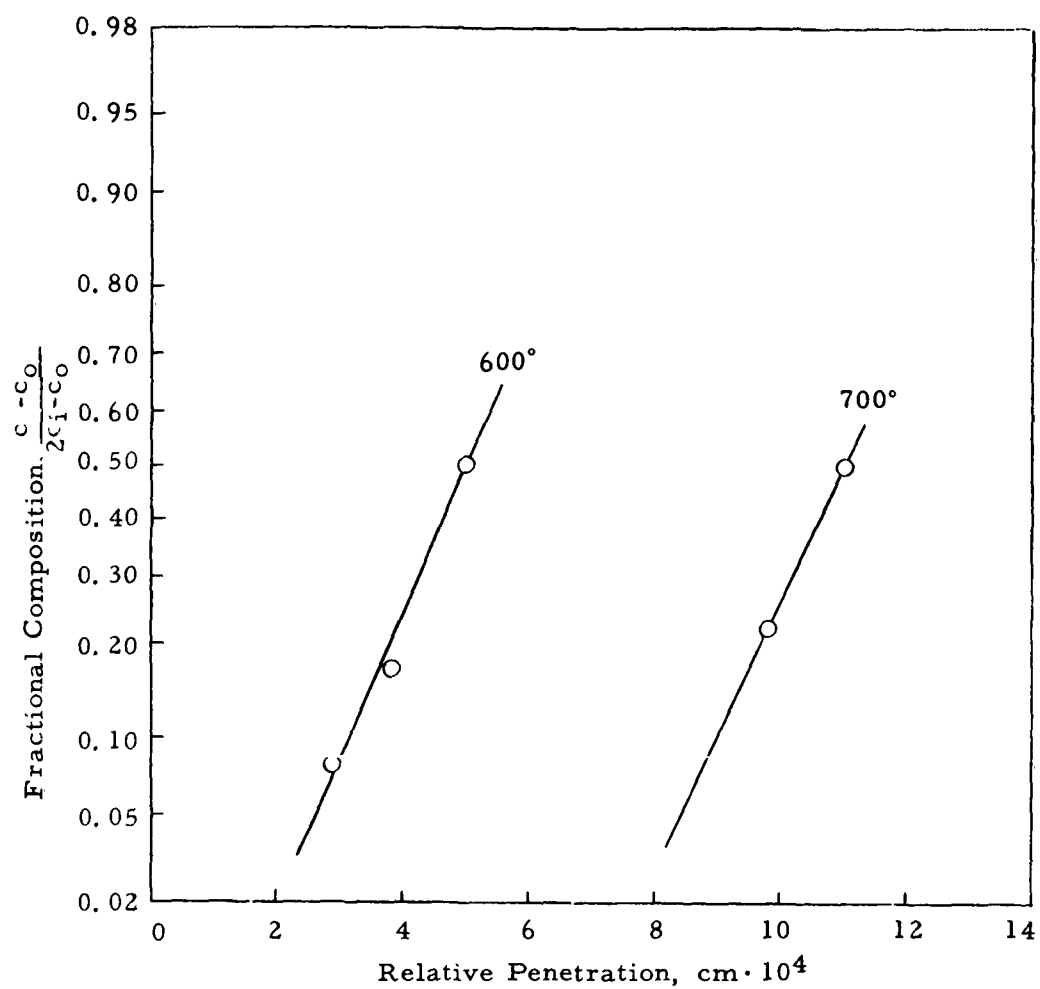


FIG. 10a - PROBABILITY PLOTS OF Ti/Ti-10V COUPLES ANNEALED AT 600° AND 700°C FOR 720 HOURS.

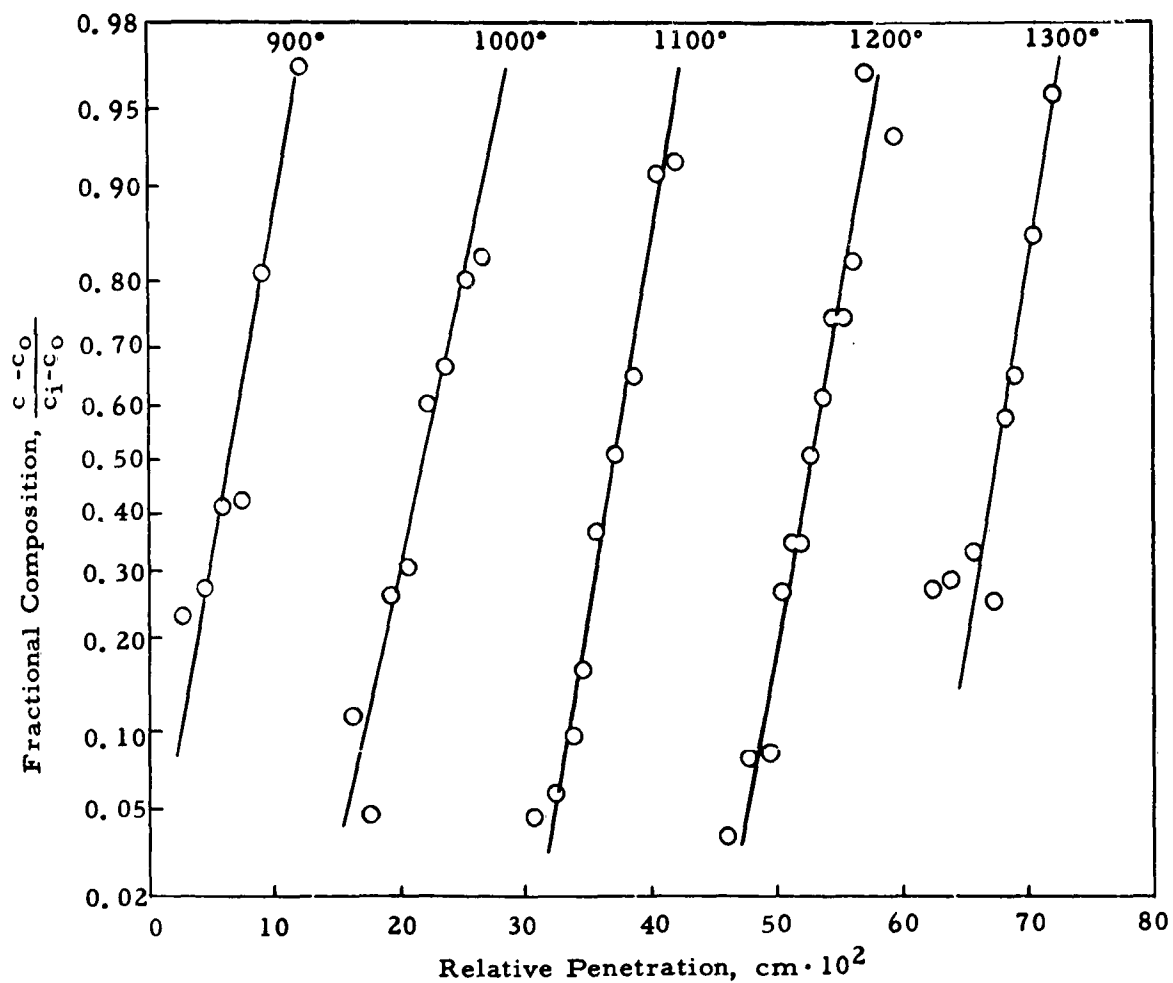


FIG. 10b - PROBABILITY PLOTS OF Ti/Ti-5V COUPLES ANNEALED AT 900°, 1000°, 1100°, 1200°, AND 1300°C FOR 520, 140, 44, 16, AND 4.4 HOURS, RESPECTIVELY.

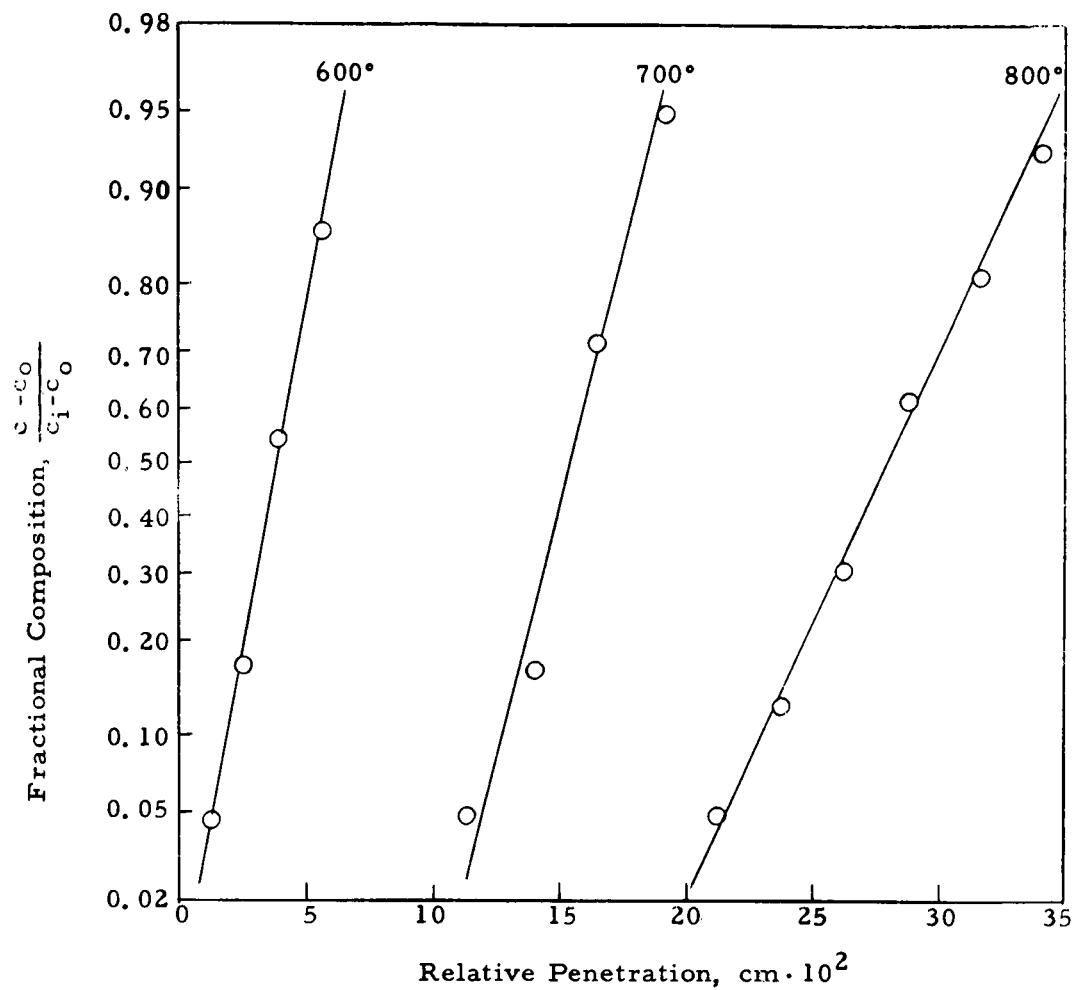


FIG. 11a - PROBABILITY PLOTS OF Ti/Ti-0.5O COUPLES ANNEALED AT 600°, 700°, AND 800°C FOR 1000 HOURS.

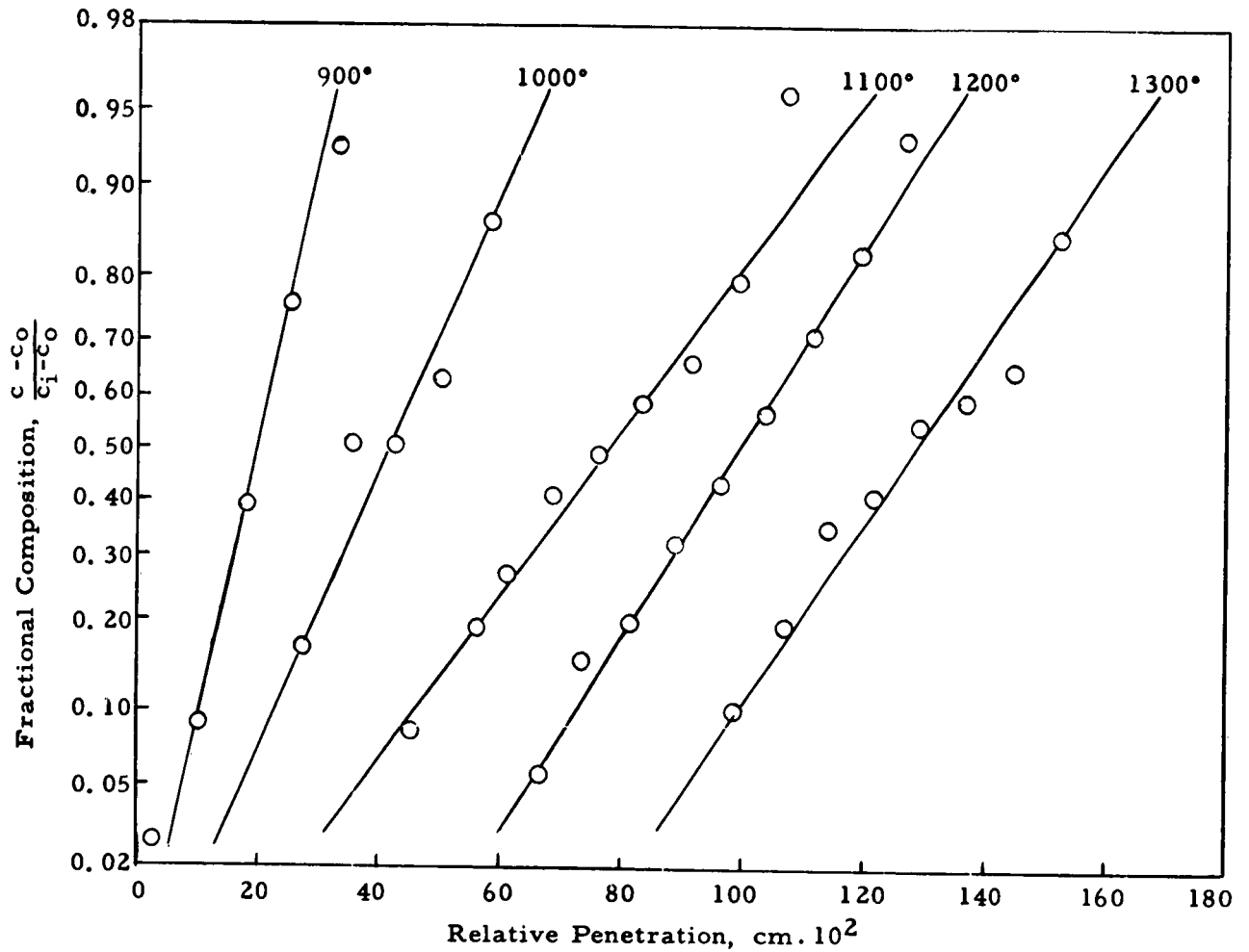


FIG. 11b - PROBABILITY PLOTS OF Ti/Ti-0.50 COUPLES ANNEALED AT 900°, 1000°, 1100°, 1200°, AND 1300°C FOR 900, 135, 48, 14, AND 4.8 HOURS, RESPECTIVELY.

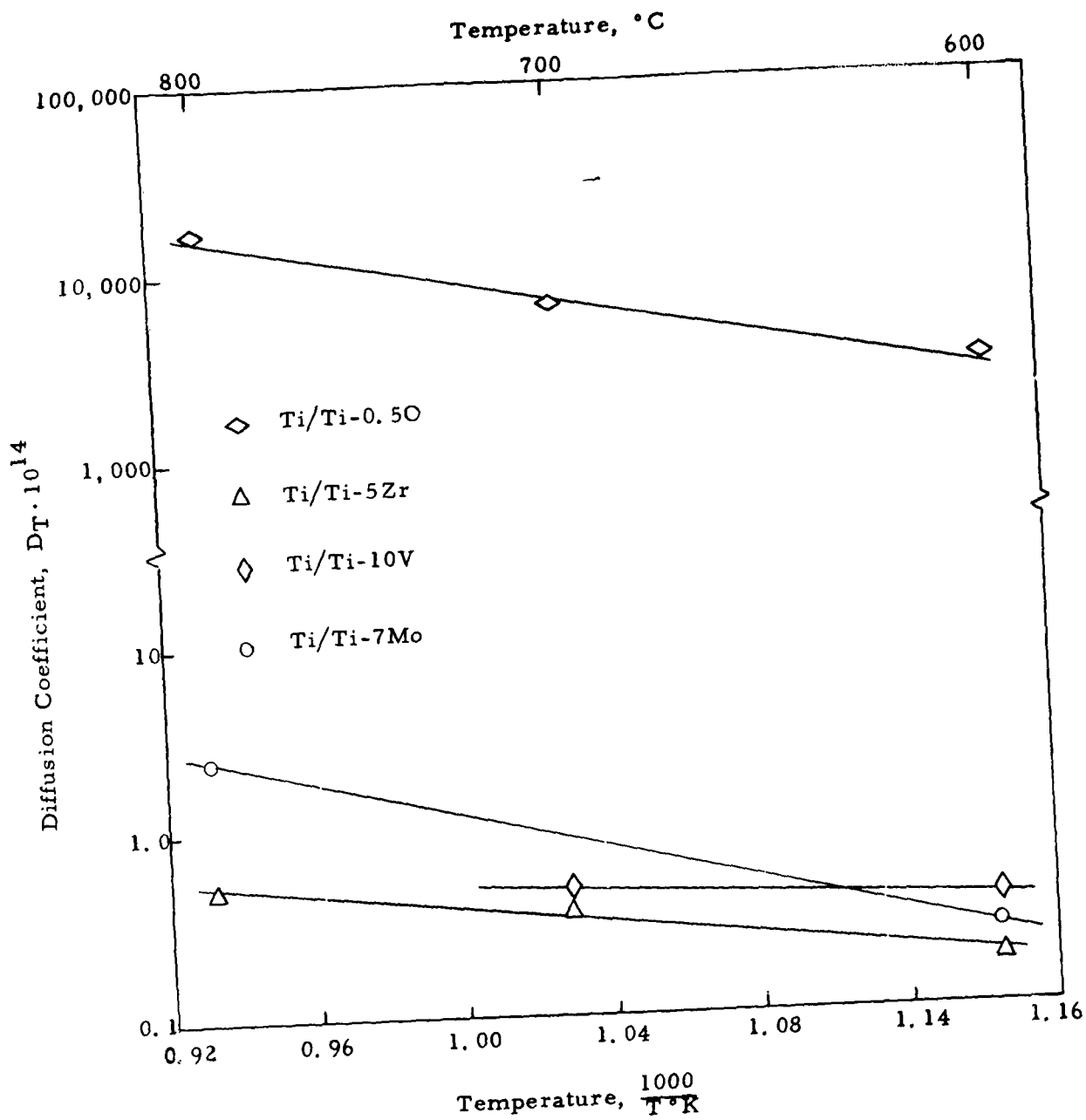


FIG. 12 - SUMMARY OF DIFFUSION COEFFICIENTS FOR ZIRCONIUM, MOLYBDENUM, VANADIUM, AND OXYGEN IN α -TITANIUM.

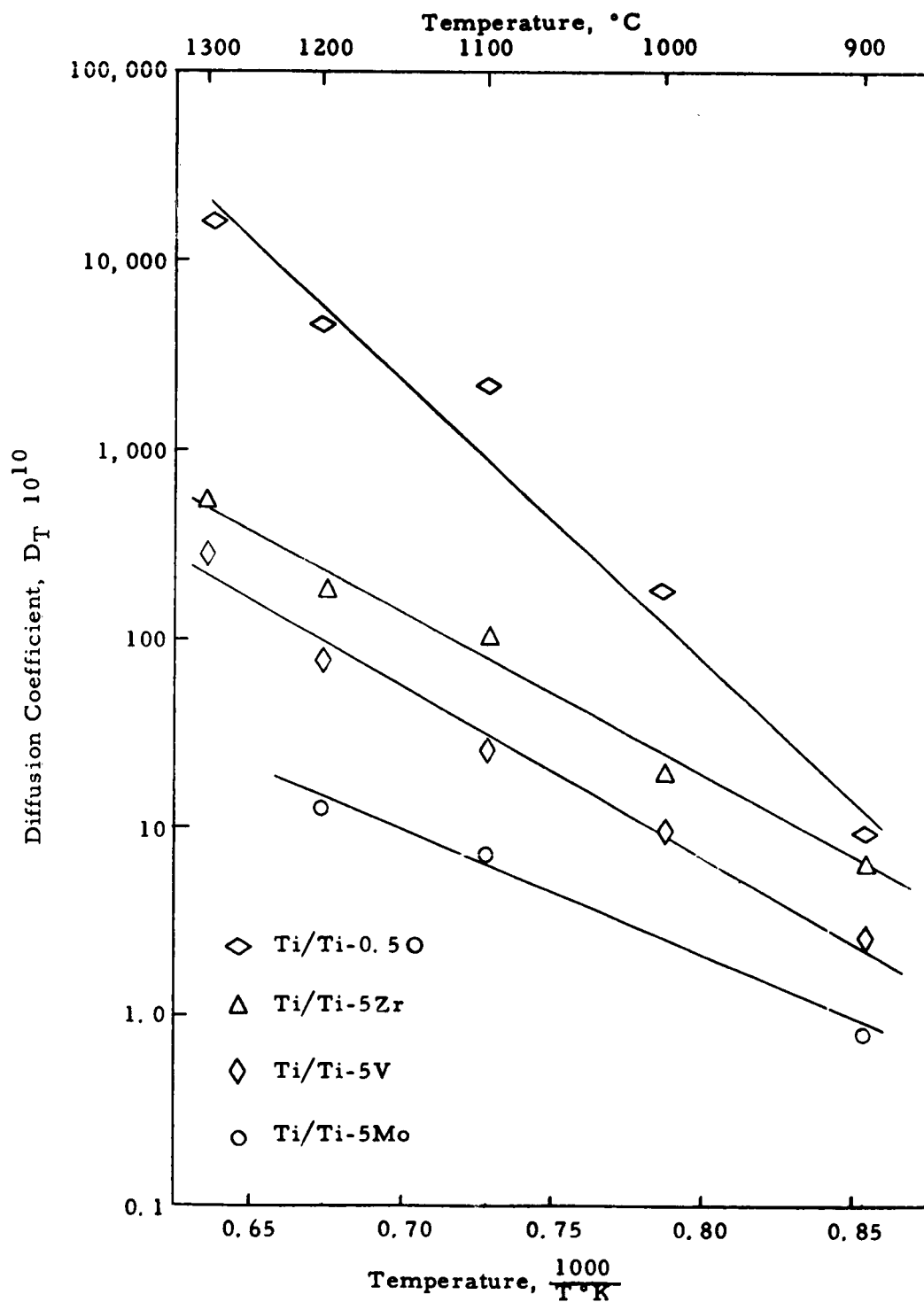


FIG. 13 - SUMMARY OF DIFFUSION COEFFICIENTS FOR ZIRCONIUM, MOLYBDENUM, VANADIUM, AND OXYGEN IN β -TITANIUM.

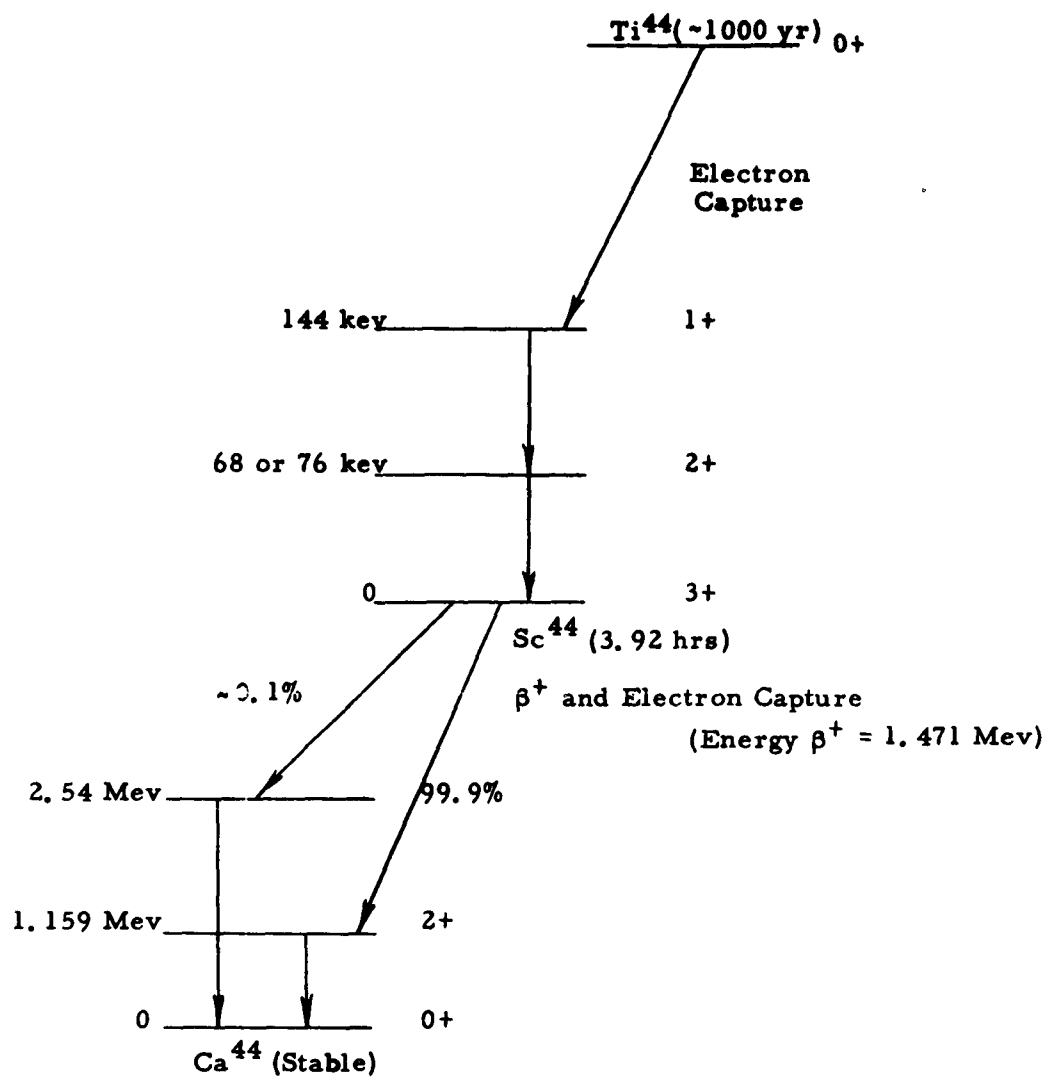


FIG. 14 - DECAY SCHEME OF Ti^{44}

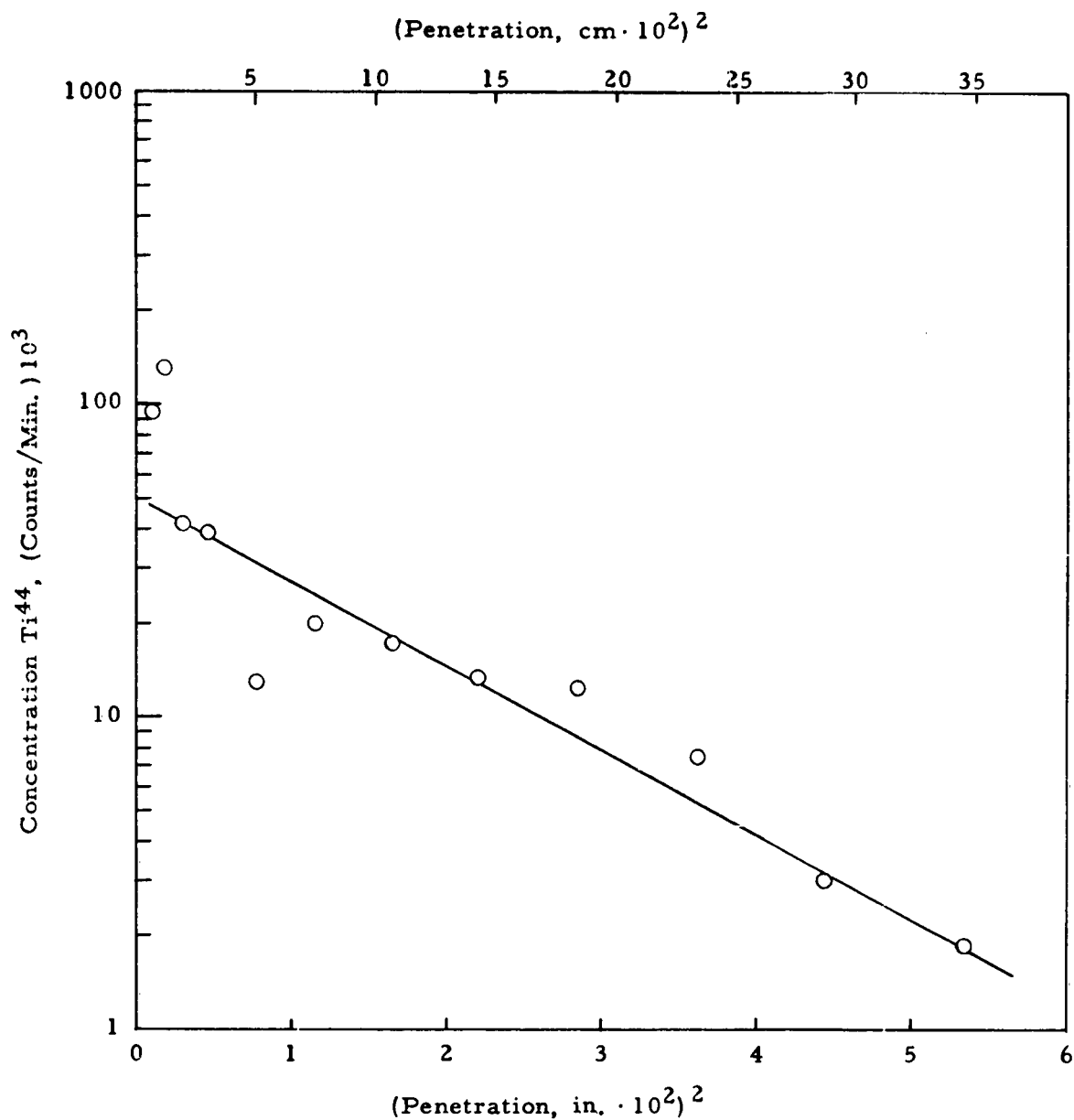


FIG. 15a - PENETRATION CURVE OF SELF-DIFFUSION COUPLE
ANNEALED AT 600°C FOR 60 DAYS.

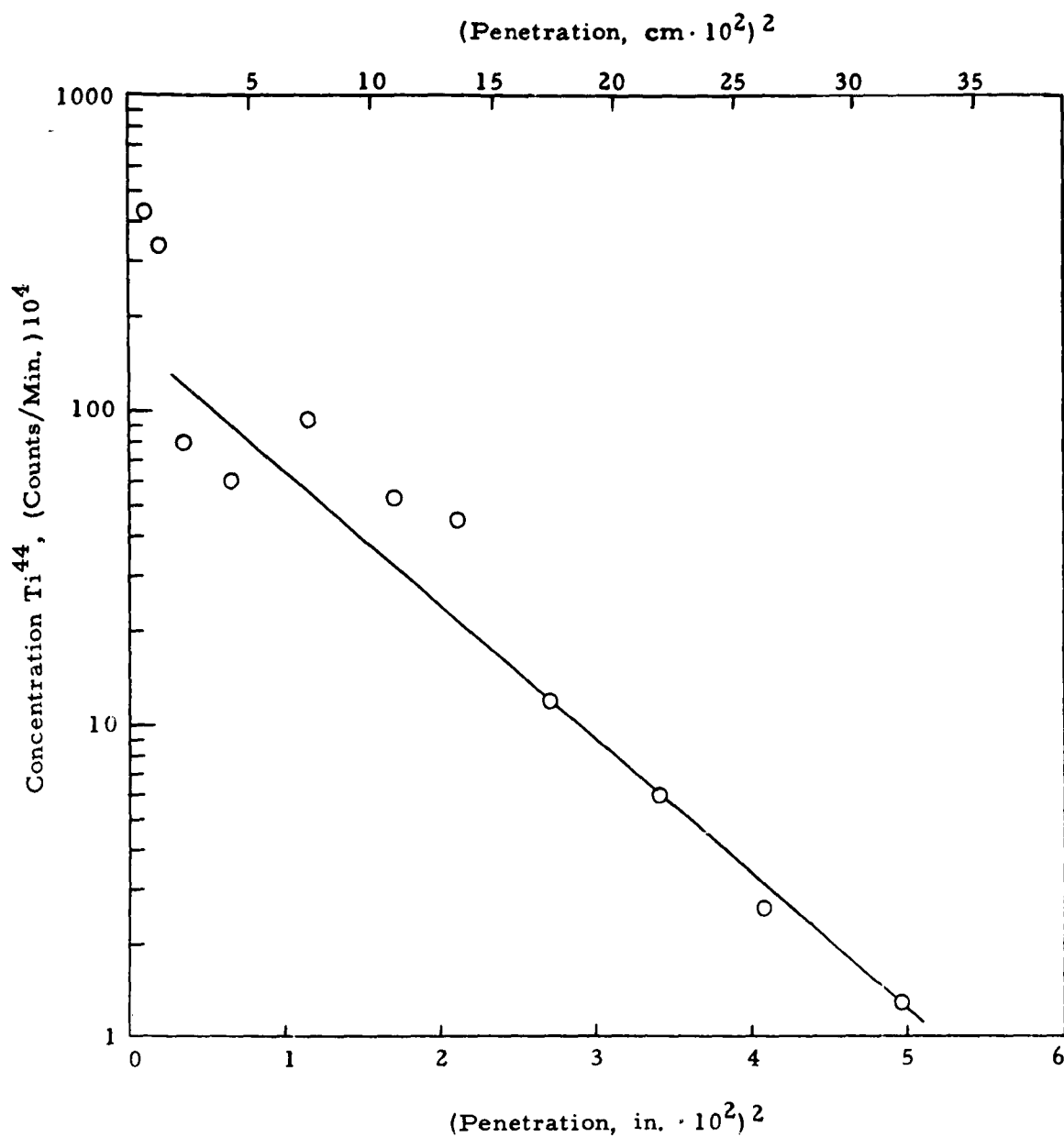


FIG. 15 b - PENETRATION CURVE OF SELF-DIFFUSION COUPLE
ANNEALED AT 700°C FOR 60 DAYS.

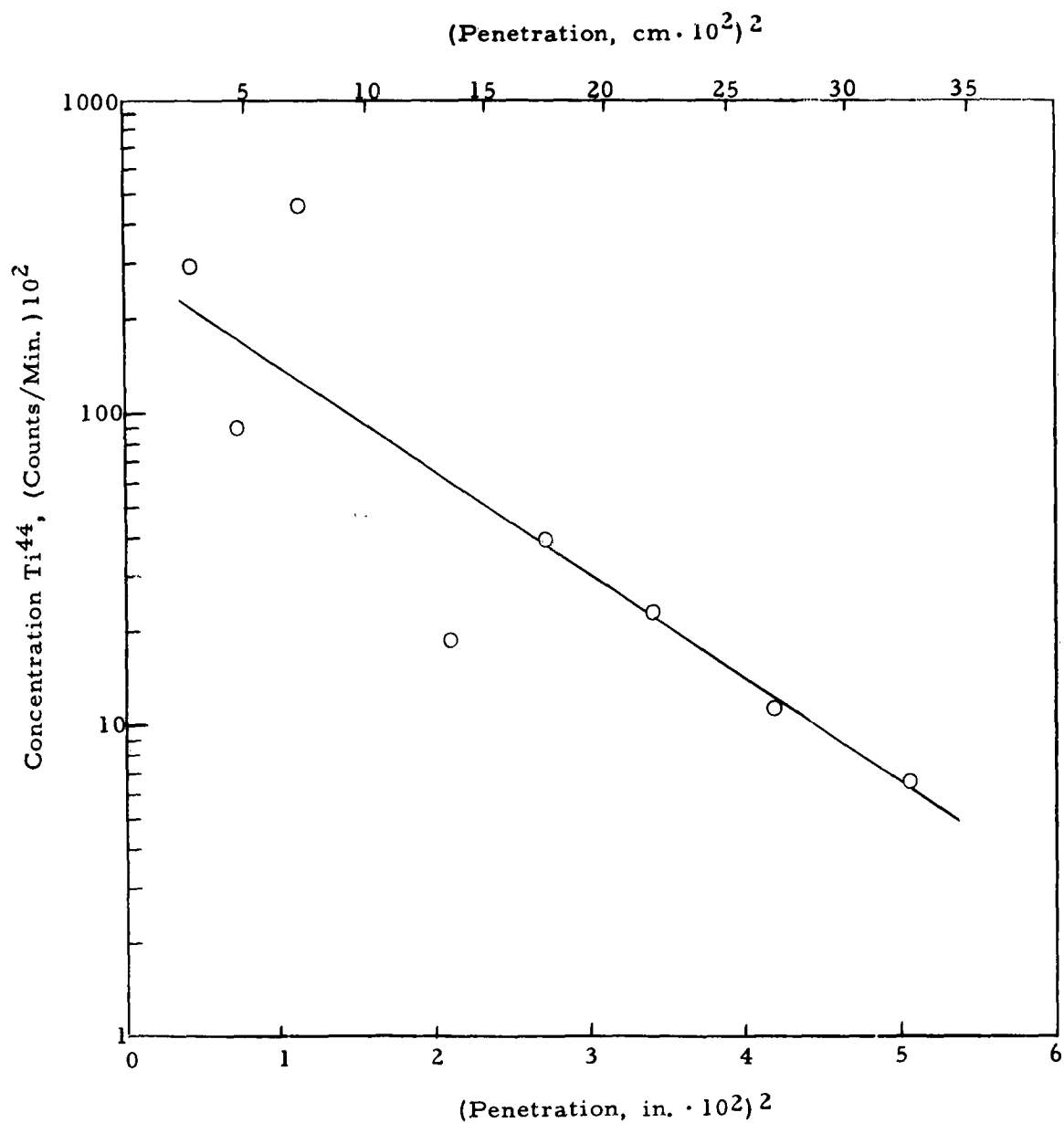


FIG. 15 c - PENETRATION CURVE OF SELF-DIFFUSION COUPLE
ANNEALED AT 800°C FOR 60 DAYS

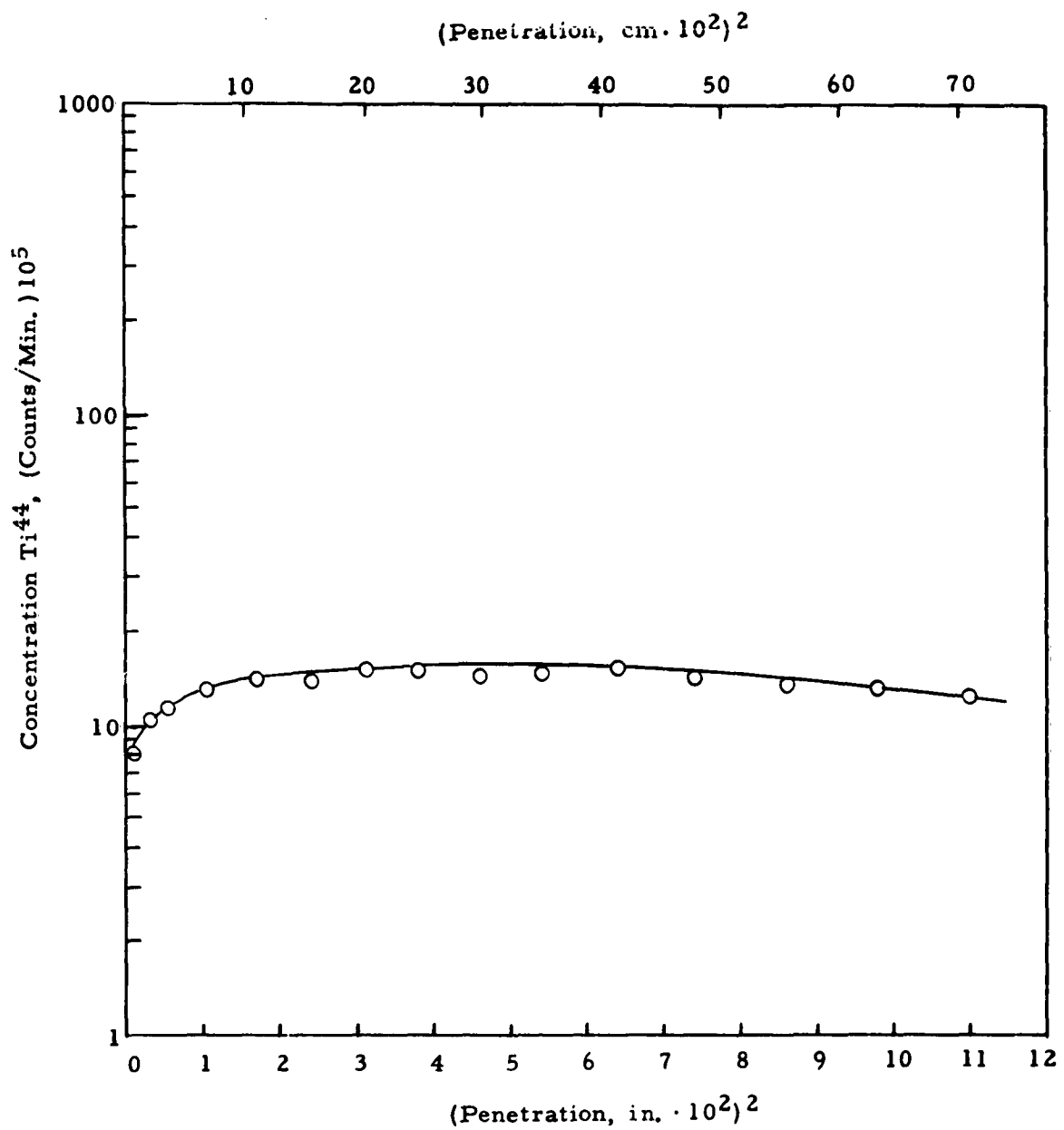


FIG. 15d - PENETRATION CURVE OF SELF-DIFFUSION COUPLE
ANNEALED AT 900°C FOR 60 DAYS.

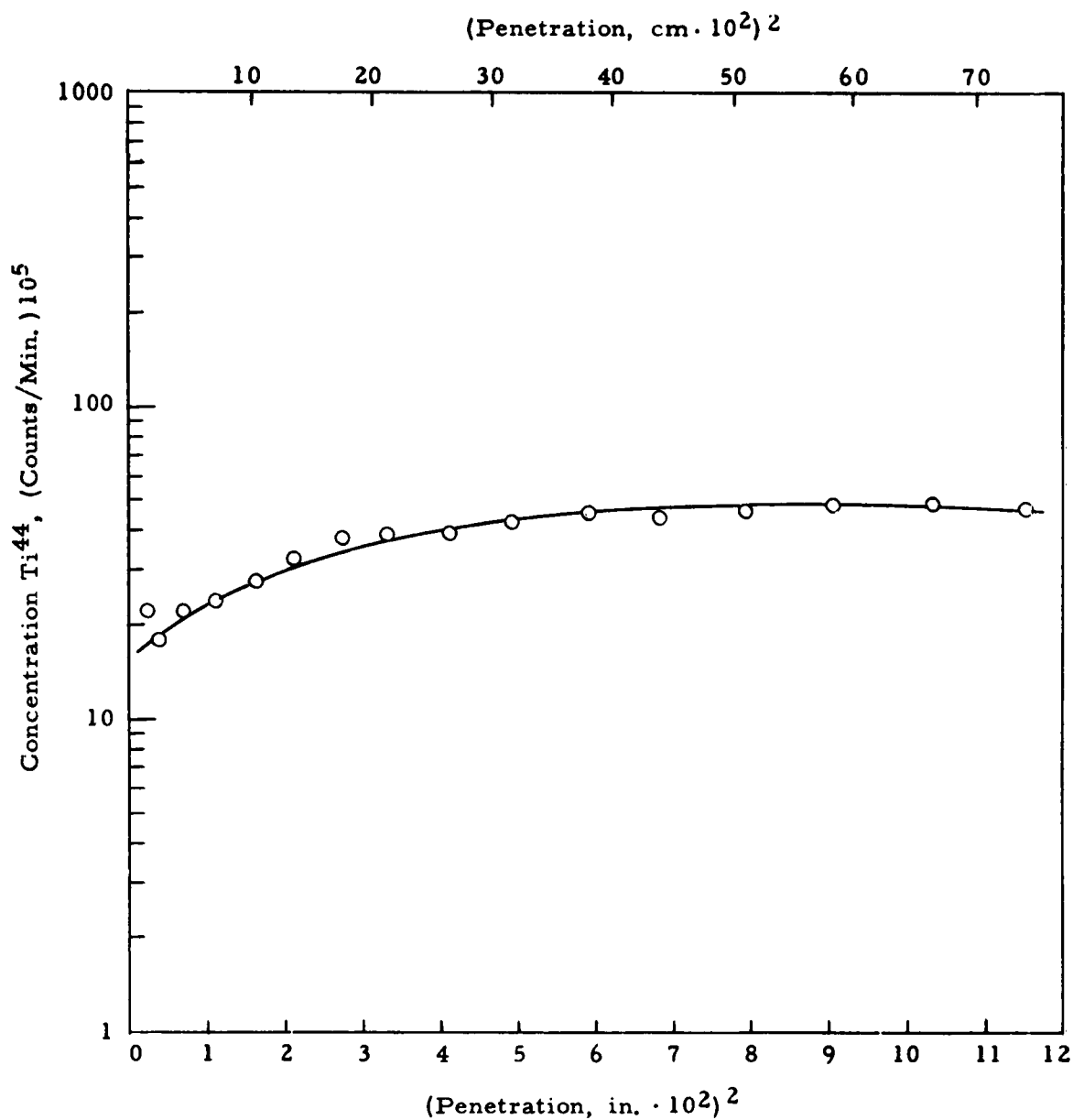


FIG. 15 e - PENETRATION CURVE OF SELF-DIFFUSION COUPLE
ANNEALED AT 1000°C FOR 30 DAYS.

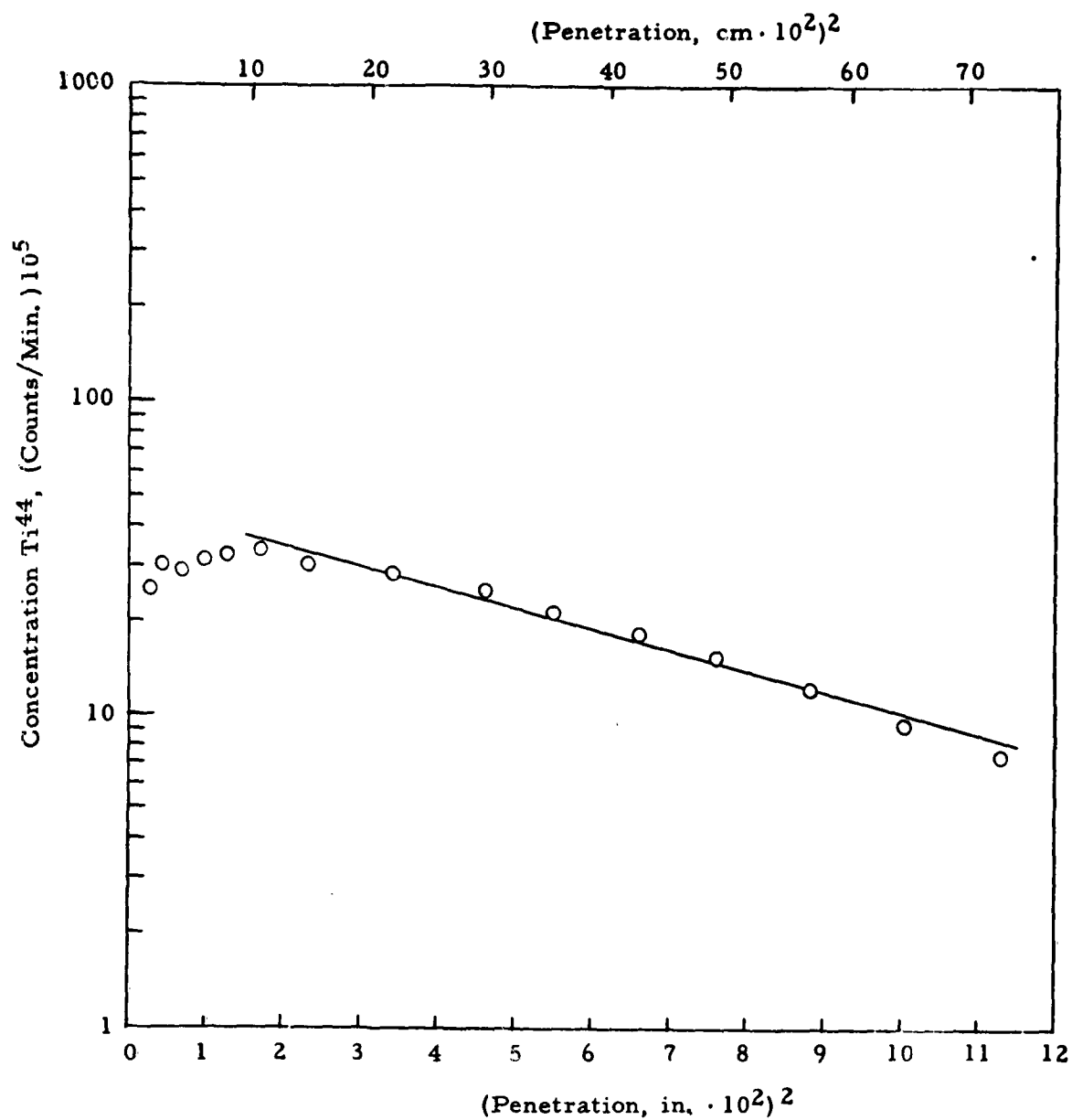


FIG. 15f - PENETRATION CURVE OF SELF-DIFFUSION COUPLE
ANNEALED AT 1200°C FOR 24 HOURS.

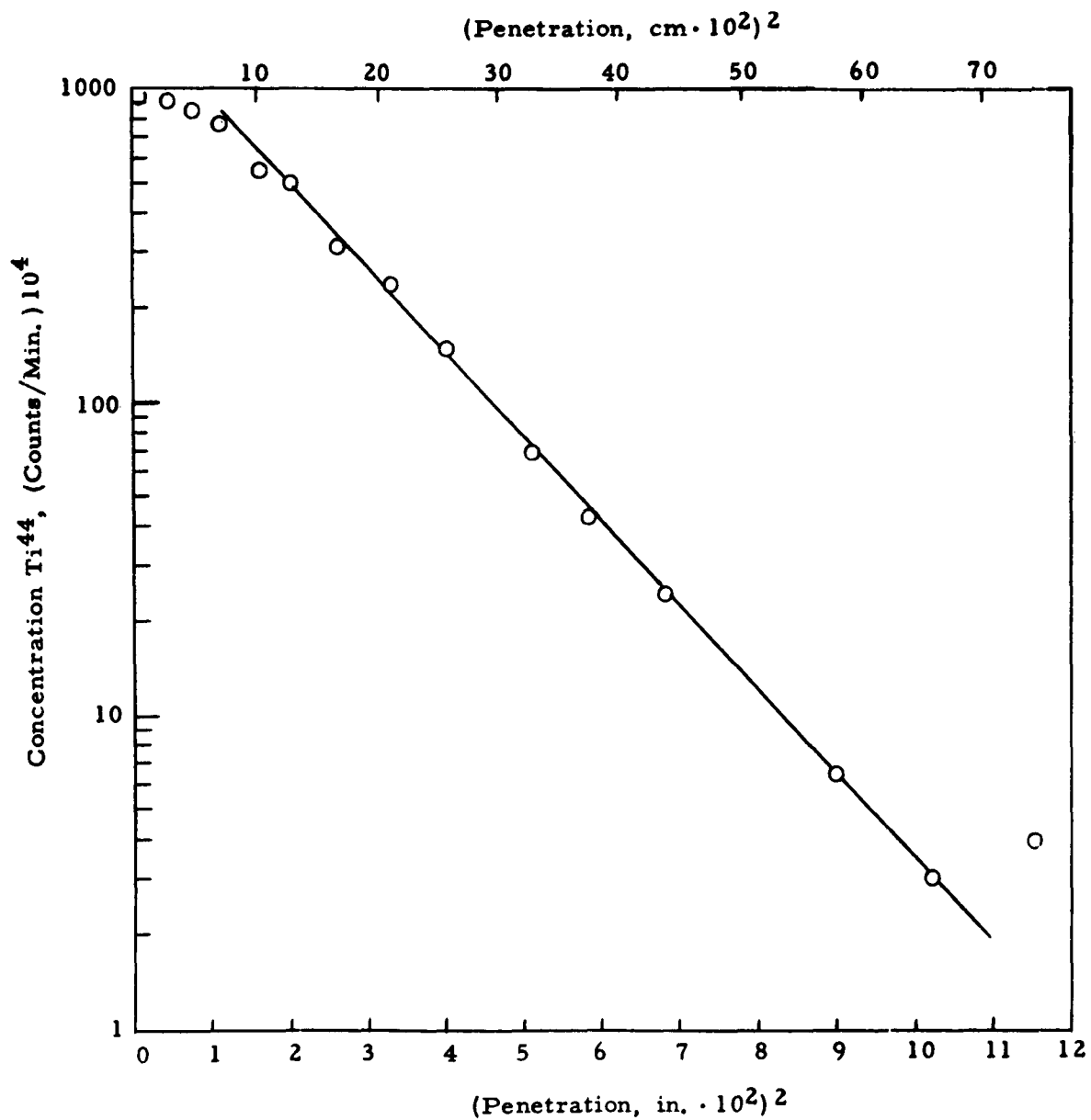


FIG. 15 g - PENETRATION CURVE OF SELF-DIFFUSION COUPLE
ANNEALED AT 1300°C FOR 3 HOURS.

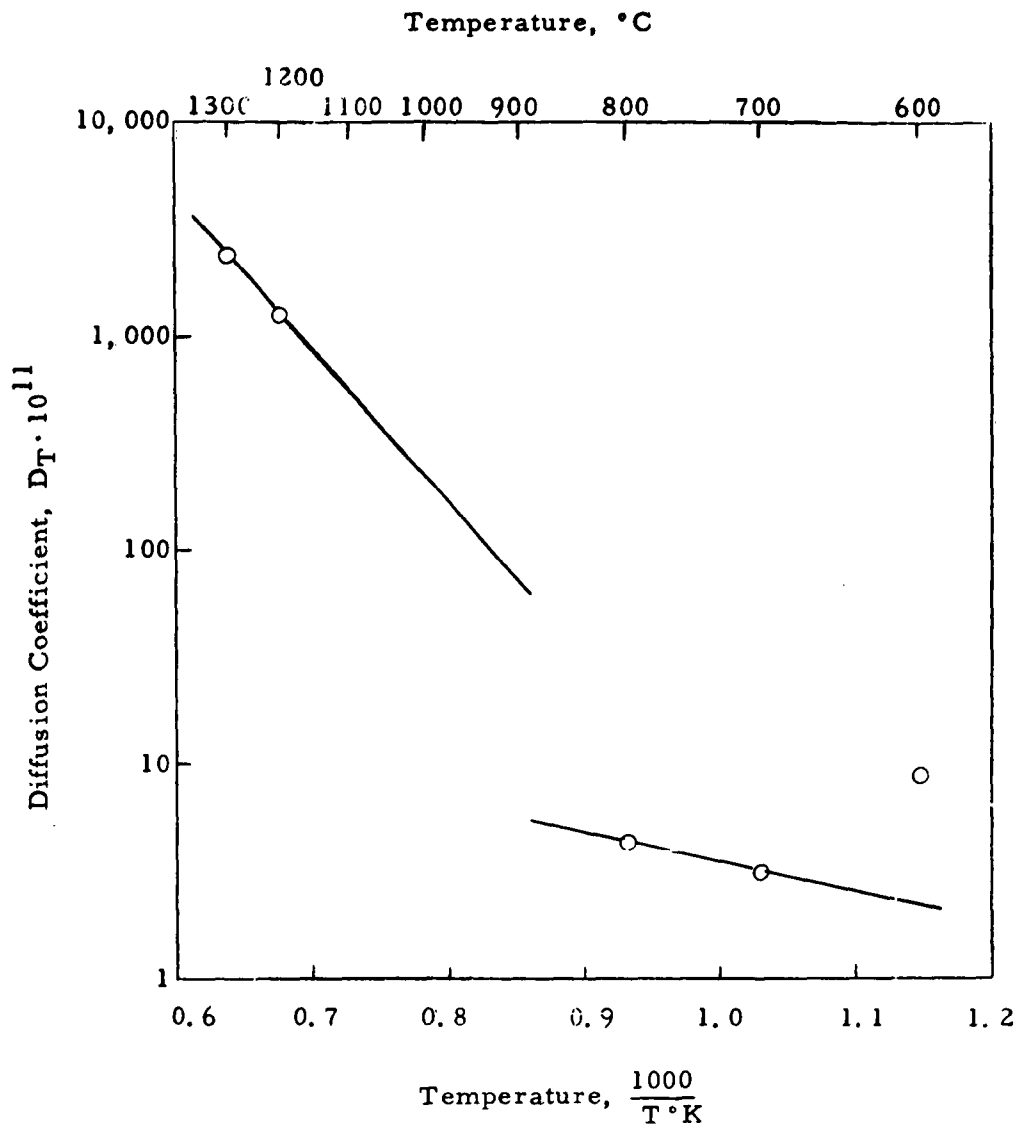


FIG. 16 - SUMMARY OF SELF-DIFFUSION COEFFICIENTS FOR TITANIUM.

APPENDIX I

THE PRODUCTION OF RADIOACTIVE Ti^{44}

By bombarding scandium with 22 Mev protons, radioactive Ti^{44} was made by the nuclear reaction $Sc^{45} (p, 2n) Ti^{44}$. The scandium metal was contained on an aluminum target.

The following procedure was developed by the Nuclear Science and Engineering Corporation to separate Ti^{44} from the scandium. Prior to being used with the bombarded sample, the chemical procedure was tested and shown to yield in excess of 90% of the Ti^{44} .

Several unsuccessful efforts were made, including those based on three solvent extraction methods, on the $NH_4OH-H_2O_2$ precipitation method, and on other precipitation methods. The successful procedure is given below.

Procedure:

The scandium was etched from its aluminum backing with HCl. Appreciable amounts of aluminum were also dissolved. After saturating the solution with HCl gas, at ice temperature, the $AlCl_3$ precipitate was centrifuged off. This precipitate was washed with HCl several times, and all liquid phases combined.

The active solution was passed through a Dowex-1 anion exchange column which had been conditioned with 12 N HCl. Under these conditions, The Ti^{44} was found to be tightly bound to the resin, while the aluminum and scandium remaining in the active solution were eluted readily by washing with 12 N HCl. Ti^{44} was finally eluted with 9 N HCl, and the volume reduced by cautious evaporation.

The Ti^{44} was coprecipitated on $Fe(OH)_3$. The precipitate was dissolved in 12 N HCl, and the resin purification repeated. The final eluate was evaporated to near-dryness and diluted to desired volume. Ten milligrams of titanium were added, and NH_4OH was added to form the hydroxide. This was filtered off and ignited at $800^\circ C$ for 30 minutes to form the TiO_2 product.

An energy spectrum of the product received from Nuclear Science and Engineering Corporation was determined at Armour Research Foundation on a 512 channel pulse height analyzer. Only activities of Ti^{44} and Sc^{44} (a daughter of Ti^{44} in the decay scheme) were observed. Thus, the purity of the product was substantiated. The yield was confirmed to be ~15 microcuries as had been stated by Nuclear Science and Engineering Corporation.

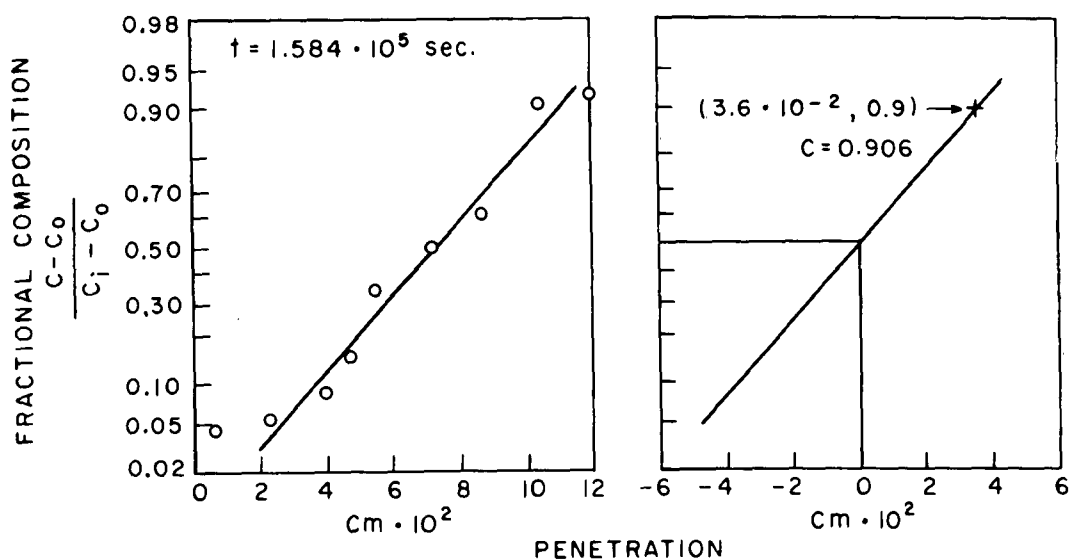
APPENDIX II

SAMPLE CALCULATIONS OF DIFFUSION COEFFICIENTS

Method II:

A typical probability plot of the penetration data for the Ti/Ti-5V couple is given at left in the sketch below as a function of the distance from the surface. From this plot, the distance origin is shifted so that the experimental data pass through (0, 0.50) as shown on the right. The diffusion coefficient, D , may now be calculated from

$$2 \left(\frac{c - c_0}{c_i - c_0} \right) - 1 = \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$$



From the right-hand plot the coordinates $(3.6 \cdot 10^{-2}, 0.9)$ are read; $c = 0.406$. This is substituted in the equation yielding:

$$0.800 = \operatorname{erf} \left(\frac{3.6 \cdot 10^{-2}}{2\sqrt{D \cdot 1.584 \cdot 10^5}} \right)$$

From a table of error functions such as that given by Pierce (33) the argument for 0.800 is found to be 0.906. Therefore:

$$0.906 = \frac{3.6 \cdot 10^{-2}}{2\sqrt{D \cdot 1.584 \cdot 10^5}}$$

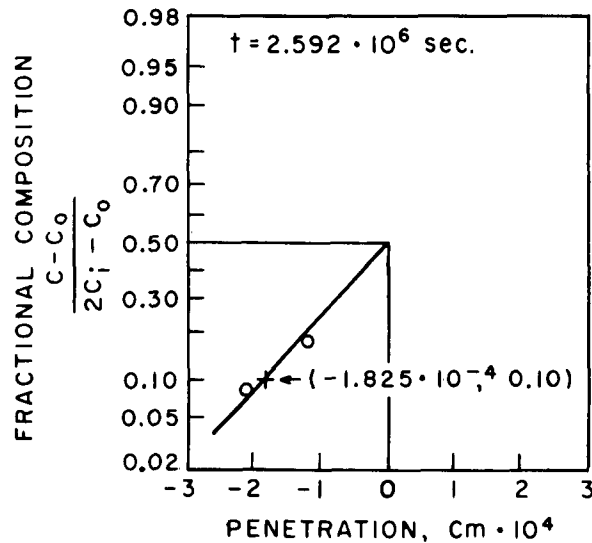
$$D = 2.49 \cdot 10^{-9} \text{ cm}^2/\text{sec}$$

Method I:

The solution of experimental data for which the mathematical boundary conditions of Method I pertain is similar to that applicable for Method II. For Method I, however, the probability function is 50% for a composition equal to the saturation composition. The pertinent solution to the diffusion equation is

$$2 \left(\frac{c - c_0}{2c_i - c_0} \right) - 1 = \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right)$$

The probability plot of the penetration curve for Ti-10V in α -Ti at 600°C is given below. The distance axis has been shifted so that the origin corresponds to 0.50.



From this plot the coordinates $(1.825 \cdot 10^{-4}, 0.90)$ are read; $c = 0.66$. Substituting in the above equation:

$$0.800 = \operatorname{erf} \left(\frac{1.825 \cdot 10^{-4}}{2\sqrt{D \cdot 2.592 \cdot 10^6}} \right)$$

The argument of this error function is 0.906.

$$0.906 = \frac{1.825 \cdot 10^{-4}}{2\sqrt{D \cdot 2.592 \cdot 10^6}}$$

$$D = 3.91 \cdot 10^{-15} \text{ cm}^2/\text{sec}$$

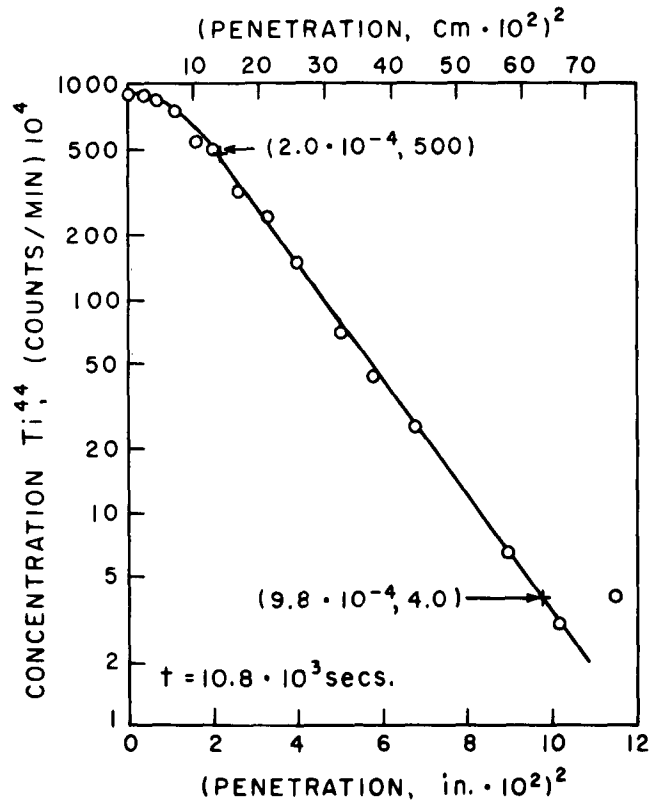
Self-Diffusion:

The self-diffusion coefficient is calculated directly from an activity-distance squared plot of the experimental data. The equation

$$\ln \left(\frac{C}{S} \right) = \ln \left(\frac{1}{2\pi \sqrt{Dt}} \right) - \left(\frac{1}{4Dt} \right) x^2$$

is pertinent. The diffusion coefficient D is calculated from the slope.

From the observed data for self-diffusion of Ti^{44} at $1300^\circ C$ we use the pair of coordinates $(2.0 \cdot 10^{-4}, 500)$ and $(9.8 \cdot 10^{-4}, 4.0)$. Since these



are expressed in common logarithms and square inches, appropriate conversion factors are applied.

$$-\frac{1}{4Dt} = \frac{\ln A_1 - \ln A_2}{x_1^2 - x_2^2}$$

$$-\frac{1}{4D \cdot 10.8 \cdot 10^3} = \frac{2.303 (\log 500 - \log 4.0)}{6.452 (2.0 \cdot 10^{-4} - 9.8 \cdot 10^{-4})}$$

$$D = 2.41 \cdot 10^{-8} \text{ cm}^2/\text{sec}$$

Aeronautical Systems Division, Dir./Materials
& Processes, Metals & Ceramics Lab,
Wright-Patterson AFB, Ohio.
Rpt No. ASD-TDR-62-561. DIFFUSION IN TITANIUM
AND TITANIUM ALLOYS. Final report, Oct 62.
57pp. incl illus, tables, 33 refs.
Unclassified Report

The self-diffusion of Ti and the interdiffusion of Al, Zr, Mo, V, and O in Ti have been investigated in the temperature range 600°-1300°C. Diffusion couples were prepared by roll-bonding or press-bonding. Electron microprobe methods were used to determine the penetration of the substitutionally dissolved penetration of interstitially dissolved oxygen.

(over)

The electron microprobe analysis could not be used to determine the penetration curves of Al in Ti because of the very high absorption of characteristic Al x-radiation by Ti.

The self-diffusion of Ti was investigated by studying penetration of Ti44, formed by bombarding scandium with protons. Diffusion couples were formed by dissolving Ti44-enriched TiO2 into the Ti.

The diffusion equations for Mo and V in α -Ti, and for the self-diffusion of Ti must be considered preliminary.

1. Diffusion
2. Titanium
I. AFSC Project 7351,
Task 735105
II. Contract AF 33(616)
-7656

III. Armour Research
Foundation,
Chicago, Illinois

IV. Rodney P. Elliott
V. Aval fr OZS
VI. In ASTIA collection

Aeronautical Systems Division, Dir./Materials
& Processes, Metals & Ceramics Lab,
Wright-Patterson AFB, Ohio.
Rpt No. ASD-TDR-62-561. DIFFUSION IN TITANIUM
AND TITANIUM ALLOYS. Final report, Oct 62.
57pp. incl illus, tables, 33 refs.
Unclassified Report

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